THE PLATINUM METALS

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I. INTRODUCTION

From 1915 to 1940 approximately eight hundred papers dealing with the inorganic and analytical chemistry of the platinum metals were published. Roughly, about 70 per cent of the number are concerned with the preparation and properties of complex compounds and with constitutional structure, and about 10 per cent with the inorganic chemistry of comparatively simple compounds. The remaining number may be classed under the subject of analytical chemistry.

The only possible logical arrangement of these papers appears to be a grouping under the leading authors. Such a grouping makes apparent the interests of these authors. Furthermore, it enables one to gain an idea of the general types of research which were pursued by a comparatively few principal investigators. By further listing the papers in chronological order, the periods of activity of the authors become evident.

The arrangement of the papers by authors likewise leads naturally to a segregation by national origin. It is observed that approximately 28 per cent of the number of papers was contributed by Russians, and approximately 24 per cent by Germans. The British Empire furnished nearly 17 per cent, the United States slightly over 10 per cent, and France about 8 per cent. The remaining 13 per cent came from Dutch, Japanese, Austrian, Italian, Swiss, Danish, Swedish, Norwegian, Latin-American, Hungarian, Lithuanian, Belgian, Czechoslovakian, Polish, and Rumanian sources.

To give even a brief survey of each paper would result only in producing an account both long and uninteresting. It seems preferable, therefore, to discuss but a few general topics and to leave the reader to consult the literature on the phases which most interest him. The attempt is made to acquaint the reader with the leading investigators and their lines of interest in the platinum metals; with the position of the United States as to production and consumption of the metals; with some of the important uses of the platinum metals; with the development in refining processes and in analytical procedures; and with the chemistry of coördination compounds of the platinum metals. This last-named subject is one about which much can be written. That phase of it which is given here is limited to the assembling of certain ideas and features, and it is written in a manner intended to familiarize the reader with the complex nature of the compounds of the platinum metals.

II. LEADING INVESTIGATORS

By arranging the literature references in the manner which has been indicated, certain investigators stand out, chiefly because they were the central figures in university research, which happens to be the main source of published work. To become acquainted with the lives and activities of some of these men is to gain a clearer concept of the state of chemical knowledge of the platinum metals, and of the directions in which this knowledge has developed.

A. RUSSIAN CONTRIBUTORS

The foremost figure of the group of Russian contributors was Ljew Alexandrowitsch Tschugajeff (born at Moscow, October 4, 1873; died at Wologda, September 26, 1922). His name is usually anglicized to Chugaev. He was educated at Moscow, taught there, and later became professor of inorganic chemistry at the University of St. Petersburg. It should be of general interest to chemists that Chugaev's first research (1) on the platinum metals, published in 1905, resulted in the discovery of the inner complex salt of dimethylglyoxime with nickel and with palladium. Since Chugaev had been trained as an organic chemist, it is not surprising that his first research on the platinum metals was one in which he studied their reactions with organic reagents. This first research was concerned with the reactions of α-dioximes with nickel, cobalt, platinum, palladium, iron, and copper. His discovery in 1918 of the brilliant red compound

$$[Os(NH_2CSNH_2)_6]Cl_3 \cdot H_2O$$

by the reaction of thiourea (13, 15) with chloroösmic acid, has provided the platinum chemist with an extremely sensitive test for osmium.

The character of practically the entire Russian output of researches on the chemistry of the platinum metals reflects the influence of Chugaev. They have consisted in the preparation and study of complex compounds of the platinum metals (principally platinum) with organic sulfides and selenides; thio-, seleno-, and telluro-ethers; methyl nitrile and isonitrile; hydroxylamine; hydrazine; aminoacetal; ethylene; methyl-, ethyl-, and diethylamines; propylenediamine; pyridine; and also of a study of various ammino and mixed ammino complexes.

Following the collapse of Old Russia, the Soviet Government created in Leningrad an organization known as the Platinum Institute of the Academy of Sciences, under whose jurisdiction subsequent work on the platinum metals was conducted. Other phases, such as refining, analysis, and study of physical properties of the metals, were included in the work of the Institute. In line with the Soviet policy of creating a Russian chemical literature, a journal was founded by Chugaev in which to publish the papers emanating from the Platinum Institute. The first issue appeared in 1920, under the editorship of N. S. Kurnakov, E. Kh. Fritzman, and O. E. Zvyagintzev. This journal, as well as the Platinum Institute, went out of existence in 1935, after which date papers appeared for the most part in a journal issued by the Institute of General Chemistry at Moscow, in a section devoted to the platinum metals (see introduction to bibliography).

Chugaev died at the age of forty-nine, and his mantle fell to Fritzman, who devoted his energies to the posthumous publication of Chugaev's accumulated researches. The principal lines of research in which Chugaev had been interested were carried on by his associates, chiefly I. I. Chernyaev, V. V. Lebedinskiĭ, and A. A. Grinberg.

A Committee on Analysis, consisting of S. F. Zhemchuzhniĭ, O. E. Zvyagintzev, B. G. Karpov, V. V. Lebedinskiĭ, N. I. Podkopaev, A. T. Grigoriev, and N. S. Kurnakov, was organized at the Institute to set up methods of analysis for native platinum, in the refining of which the Soviet Government had become vitally interested. This Committee made two reports (209, 210), one in 1926, and one in 1932, which consisted mainly of adaptations of traditional methods. Following this, Karpov published a few analytical papers, but nothing of any particular value resulted.

B. GERMAN CONTRIBUTORS

Interest in the chemistry of the platinum metals was more diversified in Germany than it was in Russia. A number of educational institutions formed centers of activity, chiefly because of certain professors. In addition, Germany possessed two of the five European platinum refineries, both of which are located in the medieval town of Hanau-am-Main.

Contemporaneous with Chugaev was Felix Alexander Gutbier (born at Leipzig, March 21, 1876; died at Jena, October 4, 1926). Gutbier was educated at the University of Erlangen, which had long been actively engaged in work on the platinum metals, particularly in the determination of their atomic weights. He taught at Erlangen from 1907 to 1912, and then at the Technische Hochschule in Stuttgart from 1912 to 1922. The last four years of his life were spent at the University of Jena. Gutbier published a great many papers, nearly all of them with students. His interests were in the colloidal platinum metals, chloro and bromo compounds of the platinum metals, the action of hydrogen and of oxygen on the metals, and an occasional research on the separation and determination of palladium.

The spirit and manner of Gutbier's researches were carried on by one of his students, Ferdinand Hermann Krauss, at the Technische Hochschule in Braunschweig. Krauss was born on August 6, 1889 at Stuttgart, received his degree at Erlangen in 1914, and, while still in the midst of a very productive scientific life, died at Köthen on June 17, 1938, after a brief illness. Krauss' interests in the platinum metals lay in the preparation and study of ruthenium tetroxide, osmium tetroxide, the halides of ruthenium and of iridium, the sulfates of rhodium, and the cyanide complexes of the platinum metals.

Another leading chemist was Lothar Wöhler (born in Bernburg, October 27, 1870). He was educated at Heidelberg and from 1911 on he directed the Chemical Institute at the Technische Hochschule in Darmstadt. Wöhler's early papers, dating from 1901, were concerned with catalytic activity and oxidation.

This early interest developed into studies of the various oxides of the platinum metals, the halides, and finally of the sulfides, selenides, tellurides, and arsenides. He also devoted attention to methods of refining and analyzing the platinum group.

Quite a different line of interest in the platinum metals was followed by Wilhelm Manchot (born at Bremen, August 5, 1869) and his students at the Technische Hochschule in München. Manchot, a student of J. Thiele, published his first paper on the platinum metals in 1903 under joint authorship with Henri Moissan. It dealt with the preparation and properties of the compound of ruthenium with silicon. Twenty-one years later, Manchot published researches on the nitrosyl and carbonyl compounds of the platinum metals. These investigations were a part of a more general one dealing with the reactions of nitric oxide and of carbon monoxide. He was also interested in the lower states of valency of the elements. The papers which dealt with uni- and bi-valent ruthenium provoked polemic discussion, principally between one of his students, Heinrich Gall (born at München, November 9, 1899), and Heinrich Remy of Hamburg.

A distinguished contributor to the chemistry of the platinum metals for a period of twenty years has been Karl Otto Ruff (born at Schwäbisch Hall, Württemburg, December 30, 1871), a graduate of the University of Berlin and since 1916 professor at the Technische Hochschule at Breslau. With a wide variety of interests in chemistry, Ruff has enriched the literature on the platinum metals with excellent papers. His chief contributions have been his studies on the oxides and halides, particularly the fluorides, of the platinum metals. His first paper (807), dealing with the oxides and chlorides of osmium and the determination of osmium in these compounds, was published in 1910.

A leading contributor to the chemistry of ruthenium from 1920 to 1928 was Heinrich Remy (born at Weeze, Niederrh., September 20, 1890), who was educated at Freiburg and since 1922 has been professor of analytical chemistry at the University of Hamburg.

Hans Reihlen (born at Stuttgart, February 2, 1892), professor of chemistry at the University of Tübingen since 1928, contributed a number of papers dealing with the stereochemistry of platinous and palladous compounds.

Quite recently, 1936 to 1938, Karl Gleu and his associates at the Friedrich Schiller University in Jena have published ten papers on ruthenium ammines. One of these papers (337) reported a new determination of the atomic weight of ruthenium, obtained by determining the ruthenium content of chloropentammineruthenium chloride, $Ru(NH_3)_5Cl_3$.

C. AUSTRIAN CONTRIBUTORS

Ludwig Moser (born in 1879; died September 26, 1930) received his doctorate at Vienna in 1905. From 1921 until his accidental death he was professor of analytical chemistry at the Technische Hochschule in Vienna. His contact with the platinum metals came as a result of a systematic study of analytical procedures for the various elements. By utilizing the reaction of bromide with bromate, he developed a procedure for hydrolyzing the chloro compounds of rhodium and iridium and thus effecting their separation from platinum.

R. Strebinger and Hans Holzer, at the Technische Hochschule in Vienna, were primarily interested in microchemical methods, including the analysis of precious metal alloys. Holzer (393) subsequently published a procedure, not microchemical, for the analysis of precious metal alloys. This procedure is not unlike that which was simultaneously developed at the National Bureau of Standards for the analysis of dental gold alloys (760).

D. DUTCH CONTRIBUTORS

The outstanding Dutch contributor was Frans Maurits Jaeger (born at Haag, Netherlands, May 11, 1877). He received his doctor's degree at Leiden in 1903, and since 1908 has been professor of physical and inorganic chemistry at the University of Groningen. His interest was mainly in stereochemical problems and those of optically active salts, which included, of the platinum metals, those of rhodium.

E. SWISS CONTRIBUTORS

Of the Swiss contributors, two are outstanding. One was Alfred Werner (born at Mülhausen, Germany, December 12, 1866; died at Zürich, Switzerland, November 15, 1919). After receiving his early education in Germany, he went to Zürich and in 1890 obtained his doctor's degree. He married and remained in Switzerland and became professor of chemistry in the University of Zürich. He devoted his talents to the problem of clarifying the concepts of the structure of complex inorganic compounds, for which he was given the Nobel Prize in 1913.

The other distinguished contributor was Louis Claude Duparc (born at Carouge, near Geneva, February 13, 1866; died October 20, 1932). Duparc received his doctor's degree at the University of Geneva in 1887. He held for many years the professorship of mineralogy, petrography, and analytical chemistry at the University of Geneva, where he also directed the Laboratory of Analytical Chemistry. His life's work, which consisted in an exhaustive study of the world's platiniferous deposits, both mineralogically and chemically, was brought into book form in 1920 under the title *Le platine et les gîtes platinifères de l'Oural et du monde* (763) and bears the coauthorship of Marguerite N. Tikonowitsch. This monumental publication is unique. Duparc's well-equipped laboratory was the chief European center of activity in the chemical analysis of platiniferous materials during the first two decades of the present century. Here H. C. Holtz in 1911 presented his doctoral thesis (791) on the composition of the principal platinum minerals of the Ural, and M. Wunder and V. Thüringer (812) applied the reagent dimethylglyoxime, discovered by Chugaev in 1905, to the separation and determination of palladium.

F. FRENCH CONTRIBUTORS

The one dominant figure among the French contributors has been Stéphane Marcel Delépine (born at Saint-Martin le Gaillard, Seine-Inférieur, September

19, 1871). Delépine received his doctor's degree at the University of Paris in 1898, where he was a student of Marcelin Berthelot. From 1913 to 1930 he was a professor at the École Supérieur de Pharmacie, and since 1930 professor at the Collège de France, Paris. Between 1905, when he began active publication, and 1939, Delépine contributed approximately forty papers dealing with the platinum metals. With but few exceptions, these papers bear only his name. His early interest in the platinum metals appears to have come about through studies of the reaction between sulfuric acid and salts of platinum and of iridium. Continuation of this interest led to an exhaustive investigation of the sulfates of iridium. He likewise investigated the chloro salts of iridium and compounds of iridium in which pyridine was introduced. One line of research was devoted to the preparation and study of the optically active oxalate complexes of iridium and of rhodium.

Students of Delépine published independently, principally in the form of dissertations appearing in the Annales de Chimie. One of these students, Raymond Charonnat, between 1924 and 1931, contributed a series of papers dealing with the stereochemistry of ruthenium.

G. BRITISH CONTRIBUTORS

The character of the contributions originating in England is quite definitely that of theoretical interest in the structure of compounds. The leading contributors have been those whose primary interests were not necessarily in the field of the platinum metals, but who came into contact with these metals because they offered possibilities for the preparation of certain types of compounds. The English contributions are further characterized by being, for the most part, those of groups of associated workers. The leading figures have been the late Sir Gilbert T. Morgan, Frederick G. Mann, Harry Dugald Keith Drew, Ernest Gordon Cox, and William Wardlaw; the leading universities, Cambridge, London, and Birmingham.

The work of Drew was confined chiefly to the disposition of the valences in platinous and palladous compounds. His conclusion was that the structure was planar and not tetrahedral. Cox and a number of his associates attacked the problem of structure with the aid of x-rays.

Mann's interest was in the preparation of compounds formed by reaction with 1,2,3-triaminopropane, β,β'-diaminodiethylamine, trimethylarsine, sulfamide, etc.

With regard to Australian, South African, and Canadian contributions, the main interests have been in mining and assaying.

An extended series of papers was published by Sir Prafulla Chandra Rây (born at Rarula, Kulna, Bengal, India, August 7, 1861; doctorate from Edinburgh, 1887; professor of chemistry at Calcutta since 1889) and his associates on compounds of platinum with mercaptanic radicals. In these compounds Rây claims that the platinum is present in both the tervalent and the quinquevalent states.

H. AMERICAN CONTRIBUTORS

At only a few universities in the United States has there been any interest in the chemistry of the platinum metals. The one outstanding figure in university circles has been Jas. Lewis Howe of Washington and Lee University at Lexington, Virginia. Howe was born at Newburyport, Massachusetts, on August 4, 1859 and educated at Amherst College. He subsequently received his doctorate at Göttingen in 1882. From 1891 until his retirement from active service a few years ago, he was head of the Department of Chemistry of Washington and Lee University.

It is always of interest to learn the circumstances which start a person along a certain line of endeavor. Professor Howe has graciously informed the writer of the remark which led him to devote his energies to the chemistry of ruthenium. Fresh from the University of Göttingen, he was looking around for a subject to work on as opportunity permitted. At a meeting of the American Association for the Advancement of Science, he happened to tell Frank Wigglesworth Clarke of his aims. Dr. Clarke remarked to him that he did not see why chemists were devoting themselves so exclusively to an element with only four valences—the main interest of chemists at that time was organic chemistry—when so much more of real chemistry could be learned from elements with more valences, especially the platinum group with eight valences. Thinking over this remark and reading the literature of the platinum metals, Professor Howe came to the conclusion that ruthenium was the most interesting metal of the group, and that it was the one of which least was known.

Howe published his first paper on ruthenium and its nitrosochlorides in 1894. His second paper, in 1896, dealt with ruthenocyanides. His third publication was a bibliography (770) of the platinum metals which covered the period 1748 to 1896. This bibliography was brought up-to-date in a second edition (686) which covered the period 1748 to 1917. Howe's interest in the bibliography has been sustained and the references collected in the period 1918 to 1940 are now in manuscript form. This painstaking task, of untold value to those interested in the platinum metals, has been carefully and faithfully done. Some way to bring this manuscript into print must be found. Its failure to become available would be a great misfortune.

Through the years Howe has continued to contribute to the chemistry of the chloro and bromo salts of ruthenium.

One of Howe's students, S. C. Ogburn, Jr., published a number of papers dealing with methods of analysis for the platinum metals. In his doctoral thesis at the University of North Carolina in 1926, Ogburn described experiments in which he tested the reactions of about one hundred twenty different reagents, some inorganic and many organic, in an attempt to ascertain their possibilities as selective reagents for the platinum metals. Scrutiny of the organic compounds used yields no inkling of what particular atomic grouping confers the property of specificity.

William R. Crowell at the University of California at Los Angeles, and Don

M. Yost at the California Institute of Technology at Pasadena, published a few papers dealing with the study of states of valency of ruthenium and of osmium.

For a time the Bureau of Mines was interested in the platinum metals, and C. W. Davis published a number of papers dealing with their detection and estimation in ores.

Before the World War the National Bureau of Standards had published a few papers which dealt with physical properties of the platinum metals. In 1917 William Francis Hillebrand, chief of the Bureau's Chemistry Division, initiated a program of chemical investigation of the platinum metals, the nature of which was the development of methods for preparing the metals in a degree of purity adequate for the most exacting requirements, and the development of methods of analysis of platiniferous materials. Since 1917 the Bureau has published approximately fifty papers. About half this number deal with the measurement of physical properties, and many of these involve the purified metals prepared in the Bureau's laboratories. Only those papers directly concerned with chemical investigations are listed in the bibliography (739 to 762).

III. Platinum Metals in the National Economy

Economic statistics concerning the platinum metals are to be found in the yearly volumes of *Mineral Resources of the United States* (773) and in *Minerals Yearbook* (774), the latter superseding the former and both being publications of the Department of the Interior, United States Government. A separate publication, *Mineral Industry* (772), edited by G. A. Roush, likewise contains economic statistics. In these publications the information is classified in quite a number of different ways.

A. PRODUCTION

In the matter of sources of the platinum metals, only a few figures will be given here to illustrate the position of the United States. The total production of crude platinum in the world up to January, 1917, was estimated to be somewhere between 8 and 11 million troy ounces. Of this amount Russia produced between 7 and 10 million ounces. Colombia was next with approximately 735,000 ounces, and Borneo third with about 200,000 ounces. New South Wales together with Tasmania had produced about 10,000 ounces, and Canada and the United States had contributed a similar quantity. Before the World War, in 1912, Russia had reached an annual production level of 300,000 ounces, which figure fell to 53,000 in 1916 and reached a low of 5500 ounces in 1921. The production in Russia has varied considerably since then and in recent years only estimated figures are available, which appear to be about 170,000 ounces or over.

Colombia, in 1912, produced 12,000 ounces. The production figure has steadily increased, with fluctuations, and in 1939 was 39,000 ounces. From 1918 on, the production has ranged between 30,000 and 55,000 ounces, the banner year being 1934.

Canada, which in 1912 was credited with the production of only 30 ounces, has risen to become one of the principal platinum-producing countries of the world, owing to the electrolytic refining of nickel and copper produced from the ores of the Sudbury District of Ontario. In 1938 Canada produced over 161,000 ounces.

The discovery of extensive lode platinum deposits in South Africa in the early 1920's, the working up of which has placed this section as a chief source of platinum, with an amount of 47,000 ounces in 1939, was a sensation in platinum mining.

Ethiopia produces a significant amount of platinum, which varies from 3000 to 8000 ounces a year.

Although the United States is by far the largest consumer of platinum metals in the world, before 1935 it contributed only a negligible quantity to the world output. For example, during the ten years 1925 to 1934 production averaged only about 8300 ounces annually—1000 ounces from placer platinum, 600 from palladium-bearing copper ore, and 6700 as by-products of gold and other metals. Since 1935, chiefly because of large-scale mining in Alaska, the production of platinum metals in the United States has advanced progressively from 11,552 ounces in 1935 to 48,269 in 1938. The latter figure is the sum of 40,932 ounces of placer platinum, 7249 ounces recovered from gold and copper refining, and 90 ounces obtained from platinum-bearing ore. Thus, the United States attained the rank of fourth largest producer of platinum metals in 1938. Although production dropped to 43,760 ounces in 1939, the United States retained its rank.

In addition to being now the fourth largest source of supply of platinum metals, the United States is an important refining center and occupies a prominent position in the international platinum trade. In 1939, for example, 41,441 ounces of new platinum metals and 63,443 ounces of secondary platinum metals were recovered by domestic refiners, 306,627 ounces of unmanufactured platinum metals was imported for consumption, and 46,329 ounces of platinum and allied metals (ingots, sheets, wire, alloys, and scrap) and a considerable quantity of placer platinum were exported.

The world production of platinum metals in 1938 was about 540,000 ounces, of which about 57 per cent was recovered as by-products in the refining of nickel, copper, and gold ores. In 1929 the world production was about 231,000 ounces, of which about 17 per cent was so obtained.

B. PRICES

Owing to market conditions, the prices of the platinum metals are liable to change suddenly.

The average price of refined platinum in New York in 1915 was $49.63 a troy ounce. In 1917 it was $102.82. After the War Department had commandeered all crude and refined platinum on March 2, 1918, a maximum price of $105 an ounce for all imports was set by the War Industries Board. The highest price paid for platinum was $154 in 1920, and the lowest, about $22, in 1933. The price averaged $36 an ounce in 1939.

Refined palladium was quoted at $70 to $85 an ounce at the beginning of 1917, but prices advanced to $130 to $135 by the end of the year. The price averaged $24 in 1939.

In the last months of 1917 iridium was sold at $180 to $185 an ounce, thereafter increasing to as much as $400 to $450 in October, 1920. It maintained a price of $260 to $280 for a considerable period. Its average price in 1939 was $112. In 1940 iridium rose from $125 to $175 an ounce, returned to $125, rose again to $140, and in December of that year brought $275. The advance in price was attributed to heavier demand by the aircraft industry, greatly reduced imports, and speculative influences.

Since 1933 ruthenium and osmium have been valued at an average figure of about $40 to $60 an ounce, respectively. Rhodium remained fairly constant during 1940 at about $125 an ounce.

C. CONSUMPTION AND USES OF THE PLATINUM METALS IN THE UNITED STATES

The most widely used metal of the group is platinum, which amounted to 63.3 per cent (100,266 ounces) of the total platinum metals sold by domestic refiners in 1939. The largest single consumer of platinum is the jewelry industry, where, alloyed with iridium, it is used as a setting for diamonds and other precious stones in rings and various other forms of jewelry. About 47 per cent (47,385 ounces) of the total sales of platinum by domestic refiners went to the jewelry trade in 1939.

Second in magnitude as a consumer of platinum in 1939 was the chemical industry, which took 20 per cent (20,306 ounces) of the total domestic sales. Platinum is used as a catalyst to produce sulfuric acid, and also as a catalyst to oxidize ammonia to produce nitric oxide and nitric acid. It is used to line processing and reaction vessels; in the hydrogenation of organic compounds; in rayon spinnerets; in spinnerets for the production of glass fiber; in nozzles for casting glass lamp bases; and in gas-analysis cells. It is also used in the form of tubing, valves, siphons, and safety disks for handling corrosive liquids and gases, and as anodes for the production of "per" salts. To chemists its use is perhaps best known in the form of crucibles, dishes, and other laboratory equipment.

The dental industry ranked third as a consumer of platinum in 1939, taking 14 per cent (13,755 ounces) of the total domestic sales. In 1940 the dental industry dropped to fourth place as a consumer, being displaced by the electrical industry. Platinum, either pure or alloyed, is used in tooth pins, bridges, and bracings for artificial teeth, as matrices on porcelain inlays, and in orthodontic appliances.

The electrical industry, the fourth largest consumer of platinum in 1939, took 12 per cent (11,952 ounces), and in 1940 became the third largest consumer. In this industry platinum is used for thermocouples, temperature-measuring and -recording instruments, precision resistance thermometers, high-temperature furnace windings, spark plug electrodes, magneto contacts, electrical contacts, relays, thermostats, automatic voltage regulators and direction indicators, and switches for potentiometric recorders.

Platinum leaf was made available during 1939 for outdoor signs, for interior decoration, and for book stamping. Palladium leaf was introduced for somewhat similar purposes in 1933.

Next to platinum, palladium is the most extensively used metal of the platinum group. It is about half as common as platinum, but less costly. Palladium comprised 32.5 per cent (51,406 ounces) of the total platinum metals sold by domestic refiners in 1939. Palladium, pure or alloyed, is adapted to many of the uses of platinum, and during the past two decades it has been employed in increasing quantities by the dental, electrical, and jewelry industries. The conservation of gold by many countries has stimulated the demand for the platinum metals, particularly palladium, and the use of palladium as a substitute for gold alloys for dental restoration, pen points, and articles of jewelry has made substantial progress. The largest consumers of palladium in 1939 were the dental and electrical industries, which purchased 22,989 and 21,510 ounces, respectively, from domestic refiners. The jewelry industry is the third largest consumer of palladium, and small quantities of this metal are used in the manufacture of chemical ware.

Iridium ranks third in consumption among the metals of the platinum group. Of the total sales of platinum metals in 1939, 2.7 per cent (4322 ounces) was iridium. This metal is used chiefly as a hardening addition to platinum, to render it suitable for laboratory vessels, surgical tools, and jewelry. At present, ruthenium is also being used as a hardening agent for platinum in the manufacture of alloys for jewelry, thus releasing iridium for other purposes.

The consumption of the other platinum metals—rhodium, osmium, and ruthenium—is small and comprised only 1.5 per cent of the total for the group in 1939. Rhodium is alloyed with platinum for high-melting-point thermocouple wire, furnace windings, and for laboratory ware for certain special purposes. Rhodium plating is employed as a finish for glassware and silverware, and in surfacing reflectors for searchlights and projectors. During 1939 platinum–rhodium spinnerets replaced the older platinum–gold spinnerets, because of their superior resistance to the various corrosive agents used in the production of rayon. Osmium, in association with other metals, provides pen points that will resist wear and corrosion by ink. These alloys also replace jewels as bearings in fine instruments. Osmium tetroxide is used as a biological stain for fats, and for fingerprint work.

IV. Properties Which Make the Platinum Metals Useful

The platinum metals owe their usefulness in commerce to a combination of intrinsic physical properties and relative chemical inertness.

The metals composing the lighter triad, namely, ruthenium, rhodium, and palladium, have densities of 12.2, 12.4, and 12.0 g./cm.^{3}, respectively. These values are slightly higher than that of lead, which is 11.34 g./cm.^{3} The metals of the other triad, osmium, iridium, and platinum, have densities approximately twice that of lead. The density of platinum is 21.45 g./cm.^{3}, and that of iridium, 22.41 to 22.65 g./cm.^{3} There appears to be some question about the density of osmium, which lies within the limit 22.41 to 22.61 g./cm.^{3} It is not definitely settled whether osmium or iridium possesses the distinction of having the greatest density of any of the elements.

In the crystalline state ruthenium and osmium belong to the hexagonal system, while the other four metals belong to the cubic system.

The crystalline fracture of fused ruthenium has a color between those of iron and platinum. Palladium is silvery white, its color being between those of silver and platinum. Compact osmium is bluish gray. Compact iridium has a brilliant grayish white surface, between those of silver and tin. Fused rhodium is white, and resembles aluminum in color. Its color is less brilliant than that of silver. The nobility of rhodium, combined with its high reflectivity, makes it particularly suitable for front-surface mirrors. The advent of rhodium plating has also made it possible to produce serviceable metal reflectors for searchlights and motion picture projectors, because a rhodium-plated surface is resistant to the combined effects of corrosion and heat.

Only in the cases of rhodium, palladium, iridium, and platinum have the freezing points of the platinum metals been accurately determined. They are, respectively, 1966°, 1554°, 2454°, and 1773°C. The melting point of ruthenium is believed to be above 2400°C., and perhaps above 2450°C., and that of osmium is believed to be about 2700°C. The estimated boiling points of the platinum metals are: ruthenium, 4900°C.; rhodium, 4500°C.; palladium, 3000–3980°C.; osmium, 5500°C.; iridium, 5300°C.; platinum, 4530°C.

The values which have been reported for the hardness of the metals depend to a great extent on the chemical purity, physical condition, and previous treatment of the metals. It is difficult, therefore, to say precisely what these figures should be. It appears that ruthenium has a hardness on the Brinell scale of about 220. That of iridium is probably slightly less than this value, and that of osmium slightly greater. The hardness of rhodium is somewhat in excess of 100, that of palladium is about 50, and that of platinum about 35. These approximate figures, at least, give an idea of the relative hardness of these six metals.

Pure platinum, which is soft, is hardened by alloying with it other metals of the platinum group. Arranged in order of their decreasing ability to harden platinum these metals are: osmium, ruthenium, iridium, rhodium, and palladium. Of these, iridium has long been the principal one used in this country. Recently, however, ruthenium has been replacing iridium in alloys intended for the jewelry trade. The ability to set precious stones in hard iridioplatinum alloys accounted for the introduction of these two metals into the jewelry industry. Iridioplatinum hypodermic needles, containing 30 per cent of iridium, have now been largely displaced by stainless-steel needles.

According to Atkinson (779) spark plug electrodes made of 20 per cent iridioplatinum give excellent results in airplane engines. The same author reports that the increase in the production of viscose rayon has led to an increased use of precious metals for spinnerets. Through the use of 10 per cent rhodioplatinum it has been possible to make a spinneret which contains 3000 holes, each with a diameter of 0.003 in. A spinneret of this kind is 1¼ in. in diameter. Thus, it has become possible to utilize ordinary textile machinery in fabricating rayon material. The same alloy is also used for "spinnerets" for producing fine glass filaments which can be woven into flexible cloth for use in electrical and thermal insulation. A recent application of the same alloy, in the lamp industry, because of its resistance to corrosion and abrasion at high temperature, has been its use in making glass-feeding nozzles for casting lamp bases.

Platinum and rhodioplatinum are in undisputed possession of the field in the manufacture of nitric acid by the catalytic oxidation of ammonia. Originally, pure platinum was used as a catalyst, but it is now being replaced by 10 per cent rhodioplatinum, which has a higher conversion efficiency and lower metal loss than has pure platinum. The production of nitric acid by the catalytic oxidation of ammonia has well-nigh supplanted natural nitrates as a source of nitric acid. Platinum catalysts, in the form of platinized asbestos, platinized magnesium sulfate, and platinized silica gel, are used to oxidize sulfur dioxide to sulfur trioxide in the manufacture of sulfuric acid.

There are three physical properties,—electrical resistance, electromotive force, and freezing point,—through the utilization of which the platinum metals enter into the measurement of temperature. The International Temperature Scale is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values are assigned, and upon specified formulas for the relation between temperature and the indications of instruments calibrated at these fixed temperatures. The basic fixed points are: the oxygen point, the ice point, the steam point, the sulfur point, the silver point, and the gold point. From temperatures of -190°C. to 660°C. the electrical resistance of platinum is made use of. From 660°C. to the gold point the temperature is deduced from the electromotive force generated in a thermocouple, one leg of which is pure platinum and the other an alloy of 10 per cent of rhodium and 90 per cent of platinum. Above the gold point the temperature is determined by means of the ratio of the intensity of monochromatic visible radiation emitted by a black body to that of the same wave length emitted by a black body at the temperature of freezing gold.

The freezing point of palladium is used as a secondary point in the scale of temperature. The freezing points of platinum and iridium have been proposed for the same purpose.

A black body maintained at the temperature of freezing platinum is under consideration as an international standard of light.

For further information on the physical properties of the platinum metals and their alloys, as well as the uses of these metals, the reader is referred to the recent book by Vines and Wise (810).

V. REFINING THE PLATINUM METALS

A. RAW MATERIALS

During the past twenty years there have been some very important changes in the platinum industry, not the least of which is the growing importance of the production of platinum from primary deposits. Whereas in 1915 the output of platinum from alluvial deposits was more than 95 per cent of the world production, by 1934 it had fallen to about 50 per cent or lower. It seems likely that the alluvial deposits will diminish in importance as the richer ones are worked out, and that future requirements will be supplied from primary deposits.

The first authentic reference to the occurrence of platinum is that of Don Antonio de Ulloa y Garcia de la Torre (777), who accompanied the French expedition in 1735 to measure the arc of the meridian at the equator. In 1748 at Madrid he published an account of his experiences, and mentioned that in the mines of El Choco, Colombia, South America, there was an infusible metallic stone which made even gold ores useless if associated with them in large quantities. Platinum was discovered in the Ural Mountains of Russia in 1819. These two localities remained the chief sources of platinum until recent years. Ural platinum, which is typical of alluvial native platinum, has the following ranges of composition: platinum, 73 to 86 per cent; iron, 8 to 17 per cent; palladium, 0.3 to 1.8 per cent; rhodium, ruthenium, osmium, iridium, 2.5 to 7.7 per cent. The recently discovered native platinum of the Goodnews Bay district of Alaska, which now rivals the Colombian output, occurs in a region geologically similar (799, 800) to that of the Urals and of Colombia.

Osmium and iridium occur native in the alloy osmiridium, which has been found in economically important quantities in the Urals, in Tasmania, and in the auriferous conglomerates of the Rand. The composition of this mineral is variable: osmium, from 23 to 40 per cent; iridium, from 21 to 35 per cent; ruthenium and rhodium together, from 9 to 15 per cent; and platinum, from 5 to 15 per cent.

Native platinum is found in regions of ultrabasic igneous rocks rich in olivine, and is recovered from stream beds and freed from gangue by mechanical treatment. For a detailed account of the geological aspects of deposits of native platinum the reader is referred to the treatise by Duparc and Tikonowitsch (763).

The sources of Canadian platinum are the well-known copper-nickel ores of the Sudbury district of Ontario. Palladium, in about the same amount as platinum, and subordinate amounts of the other platinum metals are also in these ores, besides silver and gold. These ores furnish the main supply of rhodium, which in recent years has been used to plate large reflectors and even cheap jewelry. The main sulfide mineral is pyrrhotite or magnetic pyrites, Fe_3S_4. With this is associated the copper mineral chalcopyrite or copper pyrites, $CuFeS_2$, and the nickel mineral pentlandite, NiS. The extraction of the platinum metals from the Sudbury sulfide ore constitutes an entirely new industry of rapid growth.

Platinum accompanies the nickel and copper of the Sudbury pyrrhotite in the form of sperrylite, $PtAs_2$. Palladium is present, probably as the selenide. The actual amount of platinum is, however, very small; the total platinum metal content of the ore is little more than one part in two million, that is, the platinum content is about the same as the concentration of radium in pitchblende. Owing to the fact that large tonnages of ore, over 1,800,000 tons in 1934, are treated for the recovery of the main products, copper and nickel, very substantial amounts of the platinum metals are obtained as by-products. In the treatment of the Sudbury copper-nickel deposits, the platinum metals follow the nickel through the various refining operations. The platinum metals become concentrated in the copper-nickel matte of the smelting process and, finally, when the nickel is electrolytically refined, the platinum metals remain in the anode slimes. The treatment of these ores has been discussed by Atkinson and Raper (780).

South African platinum is obtained from very extensive primary deposits in sulfide-bearing norite in the Potgietersrust and Rustenburg districts of the Transvaal. Particulars of these deposits, and methods of recovering platinum from them, are given in *Platinum and Allied Metals* (775).

In the sulfide-bearing rocks of the South African deposits, platinum occurs in both the metallic and the combined states. All the metals of the platinum group, as well as iron, nickel, cobalt, copper, silver, and gold, occur in these primary deposits. The amount of base metals is not sufficient to pay the working costs, which consequently fall mainly on the platinum metals, gold, and silver. The preliminary stage in the treatment of the ores, which contain, on the average, four to ten parts of platinum metals in one million, is that of mechanical concentration. Gravity separation yields a concentrate of metallic platinum containing up to two-thirds of the metal present, and flotation processes give a platiniferous mixture of copper, nickel, and iron sulfides which is smelted to a matte. The matte is resmelted, with the addition of sodium carbonate, under reducing conditions which lead to the liberation of a predetermined quantity of iron and nickel, into which the platinum metals pass quantitatively. The matte is allowed to weather in the air, when, owing to the presence of sodium carbonate, a friable mass is rapidly obtained from which the iron–nickel–platinum alloy can be isolated by gravity concentration and magnetic separation. If this alloy is rich in iron, it is smelted with sodium sulfate and silica; most of the iron is thereby slagged off, leaving a nickel matte rich in the platinum metals. If the alloy is rich in nickel, however, it is concentrated by smelting with sufficient sulfur-bearing material to convert 80 to 90 per cent of the nickel into the sulfide. By either method, a platiniferous alloy is ultimately obtained which can be treated electrolytically to give an anode slime for final refining by the usual wet processes.

Very few compounds of the platinum metals occur as minerals. Those which have been found are: sperrylite, $PtAs_2$; cooperite, PtS; braggite, $(Pt,Pd,Ni)S$; laurite, RuS_2 or $(Ru,Os)S_2$; stibiopalladinite, Pd_3Sb; and potarite, $PdHg$. As previously mentioned, platinum occurs in the Sudbury ores as sperrylite and the palladium probably as a selenide. In the South African ores palladium occurs, along with sperrylite, as stibiopalladinite. It is interesting to examine the variation in the relative proportions of the platinum metals in the various modes of natural occurrence. It is seen that in the native platinums the proportion of palladium to platinum is small, whereas in the platinum metals extracted from sulfide minerals the palladium is equivalent to or in excess of the platinum. On the basis of Goldschmidt's (790) scheme, the elements may be classified as siderophile, chalcophile, or lithophile, according to their equilibrium distribution between molten iron, molten sulfides, and fused silicates. The occurrence of a greater proportion of palladium in the Sudbury and South African ores than in native platinum may perhaps be correlated with the more pronounced chalcophile properties of palladium as compared with platinum.

The success of the metallurgical processes of concentrating the platinum metals in low-grade sulfide ores has depended upon the iron- and sulfide-loving character of the precious metals.

B. COMPOUNDS AND REACTIONS

The types of compounds most frequently encountered in the refining of the platinum metals are the chloro acids and their ammonium salts. The chloro acids of the platinum metals are formed when platiniferous materials are dissolved in hydrochloric acid, usually with the aid of an oxidizing agent. For example, platinum dissolves in aqua regia to form not platinic chloride, $PtCl_4$, but chloroplatinic acid, H_2PtCl_6. The anhydrous chlorides, such as $PtCl_4$, $RhCl_3$, etc., formed by the action of hot chlorine on the metals, are relatively insoluble compounds. They differ markedly from the readily soluble chloro complexes which are formed in the wet way. Chloro acids are formed by all six of the platinum metals. Depending upon the valency of the central metallic atom, different chloro acids may exist. Platinum forms $H_2[PtCl_6]$ and $H_2[PtCl_4]$; palladium, $H_2[PdCl_6]$ and $H_2[PdCl_4]$; iridium, $H_2[IrCl_6]$ and $H_3[IrCl_6]$; rhodium, only $H_3[RhCl_6]$; osmium, $H_2[OsCl_6]$ and $H_3[OsCl_6]$; ruthenium, $H_2[RuCl_6]$ and $H_3[RuCl_6]$. In the case of ruthenium particularly, as is seen later, the presence of nitric acid produces a more stable complex, in which the nitroso group is attached to the central metallic atom, for example, $K_2[RuCl_5NO]$. Osmium likewise shows this tendency.

Use is made in refining processes of the relative insolubilities of the ammonium salts of the chloro acids in which the central atom is quadrivalent. The alkali elements, potassium, rubidium, and cesium, likewise form insoluble salts, similar to those formed by the ammonium radical.

Other useful compounds are those formed when the chloro acids of the platinum metals react with sodium nitrite. The chloro acids are converted to complex nitrite compounds which, in the case of platinum, palladium, rhodium, and iridium, are $Na_2[Pt(NO_2)_6]$, $Na_2[Pd(NO_2)_4]$, $Na_3[Rh(NO_2)_6]$, and $Na_3[Ir(NO_2)_6]$. These compounds are sufficiently stable in slightly alkaline solution to permit the separation from them of many of the base metals in the form of their hydrated oxides. The ammonium salt, $(NH_4)_3[Rh(NO_2)_6]$, is sparingly soluble in neutral solution, and it is utilized in the refining of rhodium. The corresponding compound, $(NH_4)_3[Ir(NO_2)_6]$, is used in the purification of iridium.

The chloro acids of the platinum metals, except those of platinum, hydrolyze when their solutions are neutralized to an acidity corresponding to about pH 7, with the formation of hydrated oxides. Advantage is taken of this behavior to separate palladium, rhodium, and iridium from platinum.

The use of ammonium hydroxide in refining operations has been limited to the purification of rhodium, palladium, and osmium. The process of purifying rhodium by means of chloropentamminerhodium chloride, $[Rh(NH_3)_5Cl]Cl_2$, was used at one time, but it has been displaced by other methods which do not involve the formation of ammines.

In the case of palladium the use of ammonium hydroxide does have advantages. When the chloro acid of palladium is made ammoniacal and warmed, it is converted to tetramminepalladous chloride, $[Pd(NH_3)_4]Cl_2$. This compound is soluble in ammonium hydroxide. Upon adding hydrochloric acid in excess to the solution, dichlorodiamminepalladium, $[Pd(NH_3)_2Cl_2]$, is precipitated. In commercial refining operations osmium is recovered from an alcoholic alkaline solution in which its tetroxide is absorbed by converting it to osmyltetrammine chloride, $[OsO_2(NH_3)_4]Cl_2$. With these exceptions the use of ammonium hydroxide is not recommended, because of the formation of stable ammines, which can not be easily transformed again into chloro acids.

Osmium and ruthenium are distinctive metals in that they readily form volatile tetroxides, in which the metal is united with four atoms of oxygen. Osmium tetroxide melts at about 40°C., boils at 129°C., and can be distilled from aqueous solution. If pure, or in the presence of oxygen, it is stable at temperatures as high as 1500°C. (384). Ruthenium tetroxide melts at 25.5°C., but its boiling point has not been determined. At about 108°C. it decomposes with explosive violence and produces a soot, which is probably the dioxide. Like osmium tetroxide, ruthenium tetroxide can be distilled from aqueous solution. The volatilities of these two compounds are utilized in isolating them from other elements.

A word of warning should be mentioned in connection with osmium tetroxide. This substance has a deleterious effect on the tissues of the animal body. Casual exposure to it is first noticed in the eyes, which become irritated and bloodshot. One who has been exposed to the vapors of osmium tetroxide experiences an unusual optical effect. A street light, for example, appears to be surrounded by a halo in which the spectral colors are arranged in concentric bands in the order from violet near the center to red at the periphery. Superimposed upon this halo are shafts of white light which radiate from the center of the source of illumination. This latter effect is probably not caused by osmium, since those who have never been exposed to the vapor report its existence. It may be that the osmium accentuates the effect. Those who may have occasion to work with osmium should consult the publication by Brunot (753) on the toxic effects produced by osmium tetroxide.

C. METHODS OF COMMERCIAL REFINING

The chemical engineering problems in connection with the refining of platinum are of a specialized nature, with the result that experience in other fields is not always directly applicable. Moreover, the tradition of secrecy in the platinum industry up to the present has prevented refineries from pooling their experience except in a very general way. This state of affairs is in marked contrast with what is known about the plant and processes for the refining of silver and gold. Because of this tradition of secrecy concerning, particularly, the wet processes used for refining crude platinum and platinum concentrates, very few details find their way into the literature. The processes used for commercial refining, once the platinum metals have been concentrated to a point where wet processes apply, probably differ very little. The scale of operation is small; even the refining of platinum is frequently described as large-scale laboratory work, and the refining of the other metals of the group is on a still smaller scale. The separations and purifications are accomplished by a limited number of reactions. The main differences in the processes used to extract the platinum metals exist because of the particular sources of the concentrates and the relative proportions of the metals which they contain.

1. Refining of native platinum

The principal source of the platinum metals, until a few years ago, has been native platinum. This occurs as a mixture of metallic alloys in the stream beds of certain areas scattered over the world. In this form the metals are already partially concentrated by nature, and the problem of refining is one of working up this naturally occurring metallic product.

The first step in the process of refining native platinum consists in treating it with aqua regia. The treatment is continued until as much of the material dissolves as is possible. The insoluble fraction which is usually obtained consists of osmiridium, iridium, and certain non-platiniferous minerals, and is worked up separately. The soluble fraction contains the bulk of the platinum in the original material, together with palladium, gold, silver, a portion of the iridium and rhodium, and traces of osmium and ruthenium. In addition, the solution also contains iron, copper, and other base metals which have been dissolved.

(a) Precipitation of platinum by ammonium chloride

The chief component of the solution obtained by treating native platinum with aqua regia is platinum, and this is the first metal which is recovered. The usual process is to precipitate the bulk of the platinum as ammonium chloroplatinate, $(NH_4)_2[PtCl_6]$, by the addition of ammonium chloride.

To prepare the solution from this precipitation, the nitric acid and most of the excess of hydrochloric acid are removed by evaporation. A small amount of water is added to the hot sirupy residue to cause the decomposition of nitrous compounds of platinum, after which hydrochloric acid is added and the evaporation repeated. It is well to continue the evaporation each time until the temperature of the solution reaches 140° to 150°C., unless the residue becomes pasty, in which case local overheating is likely to occur. The evaporation at high temperature probably causes the reduction of part of the iridium to the tervalent state, in which form less of this element will be precipitated with the platinum salt.

After the solution has been evaporated, it is diluted to some convenient concentration,—for instance, 50 to 100 g. of platinum in 1 liter,—and set aside to permit silver chloride and other insoluble matter to settle. The solution is decanted or filtered from the insoluble residue, heated nearly to boiling, and treated with ammonium chloride. Ammonium chloroplatinate separates at once. A small excess of ammonium chloride is desirable to reduce the solubility of the ammonium chloroplatinate, but a large excess should be avoided because it increases the degree of contamination of the salt. (For more detailed discussion of the contamination of ammonium chloroplatinate by rhodium and iridium, see Section VI of this paper.) The solution is cooled quickly and filtered at once to avoid contaminating the precipitate with the very impure salt which separates on standing. The precipitate is well drained, and washed once or twice with a 20 per cent solution of ammonium chloride, after which it is dried and ignited to metallic sponge. Further purification is needed to prepare pure metal. This phase is best discussed somewhat later in connection with the preparation of pure platinum.

(b) Treatment of filtrate from the precipitation of platinum by ammonium chloride

After the precipitation of platinum by ammonium chloride, the next step depends on the nature and proportion of the other metals in the filtrate. If there is a large amount of gold, it may be desirable to separate that metal by the addition of ferrous sulfate solution. The separation is rapid and complete, and the gold thus obtained is fairly pure. If much palladium is present, it may be desirable to add more ammonium chloride and a volume of nitric acid amounting to 20 or 30 per cent of the solution. Digestion on the steam bath causes the precipitation of ammonium chloropalladate, $(NH_4)_2[PdCl_6]$, accompanied by much of the iridium and platinum in the solution. However, the presence of nitric acid interferes greatly with the removal of the remaining precious metals. Usually, the most convenient procedure is to precipitate all of the metals remaining in the solution, after the first precipitation of platinum, by means of zinc or iron. As it is very difficult to precipitate iridium completely in this way, the process must be continued for a long time, possibly for some days. Even then it is quite likely that some of the iridium will escape precipitation.

The metals precipitated by zinc or iron are washed by decantation, and, after a sufficiently large amount of such material is accumulated, it is attacked with diluted aqua regia. Gold and palladium are very rapidly attacked and platinum reasonably so. Comparatively little iridium, rhodium, and ruthenium will dissolve. If platinum predominates in the solution, it is best precipitated first, by means of ammonium chloride, as described. If not already separated, gold is then removed by precipitation with ferrous sulfate, after which palladium is precipitated as described. The various precipitates of platinum, gold, and palladium will contain more or less iridium, rhodium, and ruthenium. The remainder of these metals, together with unprecipitated platinum and palladium, are recovered by precipitation with zinc as before, after evaporating the solution to eliminate most of the nitric acid.

(c) Treatment of the residue obtained after extracting the zinc-precipitated metals with diluted aqua regia

The residue of rhodium, iridium, and ruthenium may be worked up with the osmiridium material which remained undissolved in the original aqua regia treatment of the native platinum. However, if sufficient material is at hand to work the two lots separately, it is better to do so, because the former contains little or no osmium and a very minor amount of ruthenium and may therefore be handled somewhat more simply.

If rhodium is predominant, the dried residue is intimately mixed with about 2.5 times its weight of crushed sodium chloride and brought to a dull red heat in a gentle current of chlorine. This treatment converts a large part of the rhodium to the soluble sodium rhodium chloride, $Na_3[RhCl_6]$. Some of the iridium will also be converted to a chloro salt, but this metal is less readily attacked than rhodium.

If iridium is predominant, the residue is better attacked by fusion, at 600–700°C., with three parts of sodium hydroxide and one part of sodium peroxide, in a silver, nickel, or iron dish. A portion of the iridium is dissolved, probably in the form of a basic iridate. By far the greater part of the iridium from such a fusion remains insoluble in water, but does dissolve in hot concentrated hydrochloric acid, to form chloro acids of iridium. The ruthenium will be found largely in the aqueous solution obtained by leaching the fused alkaline mass. If only small amounts of ruthenium are involved, it will be less tedious not to attempt to separate ruthenium at this point, but merely to concentrate it by precipitation together with iridium and any osmium by exactly neutralizing the alkaline solution with hydrochloric acid or sulfuric acid, adding a little alcohol, and boiling. The small amount of metals remaining in the solution after this treatment may be recovered by reduction with zinc and hydrochloric acid. The treatment of this mixture of iridium, ruthenium, and osmium is discussed in the following section dealing with the osmiridium fraction. Rhodium is not rapidly attacked by alkaline fusions. For this reason, it is often advantageous to alternate the treatments, sodium chloride–chlorine and sodium hydroxide–peroxide, until all the material has been rendered soluble.

When the material, which consists largely of rhodium and iridium, has been brought into solution as chlorides, the two metals may be separated by either of two procedures, depending on their relative proportions. Unless there is more rhodium than iridium, a convenient way of effecting the first separation is to precipitate iridium as ammonium chloroiridate, $(NH_4)_2[IrCl_6]$. Before adding ammonium chloride, the solution should be treated with a current of chlorine to oxidize any tervalent iridium to the quadrivalent state. The solution should be concentrated so as to contain not less than 50 g. of the two metals in 1 liter. Enough ammonium chloride is added to react with the iridium. A large excess should be avoided, because of its interference with the subsequent concentration of rhodium. The ammonium chloroiridate is separated by filtration, drained, and washed moderately well with a solution of ammonium chloride. It is likely to contain considerable rhodium as impurity. Most of the iridium remaining in the solution with the rhodium is recovered by evaporating the solution to dryness. This serves also to eliminate any excess of acid, which would be troublesome in the subsequent concentration of rhodium. The residue is taken up in sufficient water to dissolve any readily soluble salts, such as ammonium chloride, sodium chloride, or the complex chloride of rhodium, and filtered from the small precipitate of impure ammonium chloroiridate. The filtrate is diluted so as to contain not more than 40 to 50 g. of rhodium in 1 liter, heated nearly to boiling, and treated with sodium nitrite. This reagent first neutralizes the acid present and reacts with the ammonium chloride to form ammonium nitrite, which decomposes in the hot solution. Rhodium and the other platinum metals, as well as certain base metals, are converted to soluble complex nitrites, while other base metals, notably iron, copper, and tin, are precipitated as hydroxides. Heating is continued and more sodium nitrite is added until the color of the solution becomes yellow or light brown. The precipitate is removed by filtering and treated for the small amounts of platinum metals which it may contain. Ammonium chloride is added to the well-cooled filtrate to precipitate ammonium rhodium nitrite, $(NH_4)_3[Rh(NO_2)_6]$. The details of this treatment are described in the section dealing with the preparation of pure rhodium. The granular, white or yellowish salt is separated by filtration, washed with water and dried, or dissolved in hydrochloric acid for further purification. It is not suitable for direct ignition to metallic sponge. Residual metals are recovered from the filtrate.

(d) Treatment of the fraction of native platinum which is insoluble in aqua regia

The residue which remains undissolved in the original aqua regia treatment of native platinum is converted into soluble form by fusion with sodium hydroxide and peroxide. As the grains of osmiridium are rather slowly attacked by the alkaline fusion, they are sometimes converted to a finely divided zinc alloy by melting with five to ten parts of zinc at 600–800°C. for 2 to 3 hr. The molten mass is covered with fused zinc chloride to prevent rapid oxidation of the zinc and is occasionally stirred with a graphite rod. Treatment of the cooled, solidified melt with hydrochloric acid dissolves the excess of zinc and leaves the osmium and iridium in a finely divided residue. The powder is washed and dried, but not ignited, and is then ready for the alkaline fusion. The aqueous extract from the fusion with sodium hydroxide and peroxide contains practically all of the osmium and a large part of the ruthenium, as well as minor amounts of iridium. The treatment of the residue that is not dissolved by water is the same as that which has just been described for the separation of iridium.

The alkaline solution of osmium and ruthenium is transferred to a suitable distilling flask, strongly acidified with nitric acid, and then gradually heated to boiling. A current of air is used to carry the vapors of osmium tetroxide into a chain of receiving flasks which contain a solution of sodium hydroxide, roughly 10 per cent. Usually, a small amount of alcohol is added to the solution in the first flask. A solution of ammonium hydroxide and ammonium sulfide may be substituted for sodium hydroxide, in which case the whole solution is evaporated to dryness and the residue ignited under hydrogen to osmium sponge. Some sulfur, however, is retained by the metal.

When no more osmium tetroxide distils, as may be observed by putting a fresh solution in the first receiving flask, the contents of the several flasks are combined and digested to insure the reduction of all osmium tetroxide to sodium osmate. More alcohol is added if needed. Practically all of the osmium may be separated from the ruthenium in this distillation. It has been observed, however, that it is not possible in this way to effect a complete separation of osmium from solutions to which alcohol has been added. In some schemes of refining, osmium is recovered from the alkaline osmate solutions by adding ammonium chloride and digesting, thus converting the osmium to osmyltetrammine chloride, $[OsO_2(NH_3)_4]Cl_2$, which can be ignited to metal in an atmosphere of hydrogen. The preparation of pure osmium is discussed in a subsequent section.

After cooling the solution in the distilling flask, it is made strongly alkaline with sodium hydroxide. The solution is then saturated with chlorine, thereby converting ruthenium to the tetroxide, which distils readily when the temperature is raised to 80° or 90°C. The current of chlorine is continued during the distillation but is greatly diluted with air. The receiving flasks in this case contain hydrochloric acid diluted with four volumes of water. A small amount of alcohol is added to each receiver except the first one. When the quantity of ruthenium distilling over decreases, the solution is boiled gently and the distillation continued as long as oily droplets of ruthenium tetroxide appear in the delivery tube. Then more sodium hydroxide is added and the solution again saturated with chlorine, whereupon more ruthenium is distilled. When very little ruthenium tetroxide is obtained on repeated distillation, the remaining iridium, ruthenium, etc. are precipitated by adding a small quantity of alcohol to the neutralized solution from the distilling flask, and boiling. The contents of the receiving flasks are combined and digested to complete the reduction of ruthenium tetroxide, more alcohol being added if needed. The resulting solution is evaporated and set aside for further refining, or ruthenium may be precipitated with ammonium chloride, as described in the section dealing with the purification of this metal. In commercial processes, the evaporated solution is ignited to metal in hydrogen.

2. Operations at the Acton Refinery

The presence of relatively large quantities of platinum metals in the Canadian ores was realized for many years, and when the carbonyl process for the extraction of nickel was first introduced, at Clydach, by the Mond Nickel Company, steps were taken to recover these metals from the rich concentrates produced. In the early days these concentrates were sent to independent refineries for treatment, but later, when the production of nickel had become sufficiently large, the development of a special process and the construction of a special plant for the recovery of platinum metals became economically possible. The methods of refining initiated at the conclusion of the World War formed the basis of the operations conducted in the refinery which was built at Acton (London, N.W. 10) in 1924.

Later, in addition to the concentrates from the carbonyl process, crude platinum from South Africa was also treated. More recently, the treatment of concentrates from the electrolytic nickel refinery at Port Colborne, Ontario, has been undertaken at Acton. The Acton Refinery of the Mond Nickel Company is the largest platinum metals refinery in the world.

Johnson and Atkinson (795) have described the operations carried on at the Acton Refinery. The residues from the Clydach refinery, which contain about 4 per cent of platinum metals in addition to silver and gold, require further concentration before the platinum can be extracted economically with aqua regia.

The refining of the richer concentrates from the nickel and copper refineries, which contain more than 50 per cent of platinum metals and very little silver, commences with the treatment with aqua regia.

For further concentration, the residues containing 4 per cent of platinum metals are smelted with litharge, fluxes, and charcoal in small tilting furnaces, with basic linings, to collect the precious metals and at the same time to slag off silica and base metals. The principal reaction during smelting is the reduction of lead oxide to metallic lead, which acts as a collector of the precious metals. Another important reaction is the conversion of lead sulfate, which forms approximately 50 per cent of the Clydach residue, to lead carbonate by means of sodium carbonate. The lead carbonate immediately decomposes into lead oxide and carbon dioxide. The sodium sulfate separates in the molds as a top slag, which is removed and leached. Subsequent cupellation of the ingots in smaller furnaces removes the excess of lead as litharge, which is used again in further smelting charges, and yields a precious-metal alloy about five times as rich in silver as the Clydach residue. If lead alloys are cupelled to a finish, that is, until litharge ceases to form, there is a probability of producing a cupelled metal which is not readily attacked in the course of subsequent refining operations, hence the reason for partial cupellation.

The alloy formed on cupellation is treated with boiling concentrated sulfuric acid, which removes most of the silver and about one-third of the palladium as sulfates. The residue contains the platinum, gold, and the rest of the palladium in a form particularly suitable for extraction with aqua regia, which is the next operation. From the solution of chlorides thus obtained, the gold is precipitated by ferrous sulfate, and then the platinum as ammonium chloroplatinate by the addition of ammonium chloride, and lastly, the palladium is precipitated as dichlorodiamminepalladium. The only one of these operations which calls for special comment is the precipitation of dichlorodiamminepalladium. The palladium chloride is converted into soluble tetramminepalladous chloride, $[Pd(NH_3)_4]Cl_2$, by the addition of excess ammonium hydroxide. Upon acidification with hydrochloric acid, the sparingly soluble yellow dichlorodiamminepalladium, $[Pd(NH_3)_2Cl_2]$, is precipitated. The impure salt is purified by dissolving it in ammonium hydroxide and reprecipitating it with hydrochloric acid. The salt thus purified is ignited to metallic sponge. The impure ammonium chloroplatinate which is first obtained is ignited to metal, redissolved in aqua regia, and reprecipitated. Ignition of this salt yields platinum sponge. The silver and gold are purified electrolytically, by the Moebius and Wohlwill processes, respectively, special attention being given to the recovery of small amounts of platinum metals.

All liquors resulting from the processes are treated with zinc, or iron, and acid to recover traces of the precious metals. In practice, it is found to be more economical to smelt the final insoluble and reduction residues than to attempt to recover rhodium, ruthenium, and iridium from them by wet processes. The lead ingots obtained by smelting are cupelled to remove excess lead, and the resulting precious metal alloy is parted with nitric acid. The solution is treated in order to recover precious metals, especially palladium, platinum, and silver, which dissolve during the operation. Most of the rhodium, ruthenium, and iridium initially in the lead alloy are concentrated in the insoluble residue, from which they can be extracted and refined by chemical processes. Rhodium is extracted by fusing the concentrate with sodium bisulfate. Subsequently, the rhodium is refined by a modification of the process described by Wichers, Gilchrist, and Swanger (747). The insoluble residue from the bisulfate fusion is given appropriate treatments to remove platinum, gold, and lead sulfate, as a result of which a concentrate of ruthenium and iridium is obtained. This concentrate is fused with caustic potash and potassium nitrate in spun-iron bowls at a dull red heat, which converts the ruthenium into soluble potassium ruthenate. The cakes are then dissolved in water; after settling, the clear solution is decanted into glass flasks and treated with chlorine. The tetroxide of ruthenium which is formed is absorbed in diluted hydrochloric acid containing methyl alcohol. Evaporation of the contents of the absorption vessels gives an oxychloride, $RuOCl_2$, which is reduced to metal by igniting in hydrogen.

There appears to be very little osmium in the precious-metal concentrates received from the nickel refineries. It amounts to less than 1 per cent of the ruthenium content, and on account of the similarity in properties of these two metals it will be found as an impurity in the ruthenium unless it is eliminated, which can easily be done by heating the ruthenium oxychloride to dull redness in a current of air. The resulting osmium tetroxide is absorbed in an alcoholic caustic soda solution and the osmium finally recovered as osmyltetrammine chloride, $[OsO_2(NH_3)_4]Cl_2$, which can be ignited to metal in an atmosphere of hydrogen.

The caustic fusion, besides converting the ruthenium into potassium ruthenate, which is soluble in water, also converts the iridium into an oxidized form which, although insoluble in water, is dissolved in aqua regia. The chloride solution thus obtained is evaporated, and a crude ammonium chloroiridate obtained by adding ammonium chloride and oxidizing with small amounts of nitric acid. The crude salt is separated from the accompanying ammonium chloroplatinate by fractional crystallization; the use of a mild reducing agent facilitates the solution of the iridium salt. Recrystallization is continued until the desired purity is achieved; the salt is then decomposed by heating in a gas-fired muffle furnace. The partially oxidized metal is reduced by heating in hydrogen and is further purified.

The average purities of the metals recovered from the crude concentrates from the refining of nickel are as follows: platinum, 99.93 per cent; palladium, 99.94 per cent; iridium, 99.7 per cent; rhodium, 99.7 per cent; ruthenium, 99.7 per cent; gold, 99.97 per cent; and silver, 99.97 per cent. In practice, not more than 0.25 per cent of the platinum metals contained in the concentrates is lost, while 1.25 per cent is temporarily retained in furnace slags, which are returned to the nickel refinery for retreatment. The remaining 98.5 per cent is produced directly as refined metal. The losses occurring in the processes of extracting the nickel and copper are also very small, and it is estimated that 90 per cent of the precious metals, probably excepting osmium, contained in the ore is ultimately recovered.

In the wet-process plant of the Acton Refinery chemical stoneware is the material most generally used for the construction of vessels for refining processes involving the use of acids, the two principal types of vessels being mixers or vats up to 100 gallons capacity, and vacuum filters up to 80 gallons capacity.

Aqua regia treatment of concentrates is normally conducted in steam-heated chemical stoneware vessels, each of 140 liters capacity. A temperature of 90°C. is readily obtained, which is adequate for dissolving the finely divided platinum, palladium, and gold contained in the residues. Working under these conditions, there is a further advantage that there is no risk of bumping when heavy insoluble matter settles to the bottom of the vessel. On the other hand, the conditions are quite different for dissolving mineral platinum, which is best done in gas-heated Vitreosil bottles of 70 liters capacity, using concentrated aqua regia at or near the boiling point. Evaporation of nitric acid solutions is done in similar Vitreosil bottles equipped with condensers suitable for the distillation of mineral acids.

Nitric acid treatment is carried out in gas-heated 20-liter basins made of Vitreosil, which are also used for bisulfate fusions. Sulfuric acid treatment is done in pans made of fine-grained gray cast iron, each of 25 liters capacity, and heated by gas. Both lead-lined wood tanks and iron vessels are used for liquors containing free sulfuric acid.

Wooden tanks up to 300 gallons capacity, lined with soft rubber, are satisfactory for some of the operations, for instance, reactions in which sufficient free hydrochloric acid is present to make lead-lined vessels unsuitable. Acid-resisting hose is used to convey acid liquors and to make connections for removing fumes from reaction vessels. Steel vessels lined with hard rubber are preferred to chemical stoneware vessels for operations involving the use of hydrochloric acid in which the heat of reaction causes a rapid rise of temperature. Porcelain ware is used for small-scale purification work.

Decomposition of ammonium chloroplatinate, at the rate of 50 kg. a day, is accomplished in Vitreosil trays which are slowly heated in muffle furnaces fired by gas. Particular care must be taken while heating the material from 310° to 370°C., after which the temperature is raised to 900°C. to complete the removal of volatile matter. Dichlorodiamminepalladium is decomposed in a similar way. The fumes evolved from the decomposing salts are drawn away through a Cronite tube (an alloy containing nickel, chromium, and iron) into a sublimate box, care being taken that the tube does not become choked with condensing ammonium chloride.

The principal feature of the wet-process plant is that the vessels are arranged on terraces. Successive steps of a process can be arranged in a line from top to bottom with gravity flow of the liquor from one vessel to the next.

D. METHODS USED AT THE NATIONAL BUREAU OF STANDARDS FOR THE PURIFICATION OF THE PLATINUM METALS

The preparation of the platinum metals in a highly pure form suitable for the determination of various physical properties, etc., requires description additional to that given for the production of metals of commercial purity. An early phase of the work on the platinum metals at the National Bureau of Standards, at a time when neither the highly pure metals nor information concerning their preparation was available, was the development of methods for preparing the metals in a degree of purity adequate for the most exacting requirements. These methods are given in condensed form in the following paragraphs. For details the original publications (747, 754, 757) should be consulted.

1. Platinum

(a) By repeated precipitation as ammonium chloroplatinate

Of the methods that have been used for the purification of platinum, repeated precipitation of ammonium chloroplatinate has been the most important and the most widely used. The salt is relatively insoluble. It may be readily precipitated in a form that is easily filtered and washed, and it may be directly converted to metallic platinum by ignition. Any desired degree of purity may be attained by a sufficient number of reprecipitations. However, the number of precipitations required to produce a very pure metal, such as that used for thermocouples and resistance thermometers, is somewhat surprising. It might be expected that in this, as in other processes of purification by recrystallization, the principal cause of difficulty would be the formation of other salts which are isomorphous with that of platinum, especially if they are of the same order of solubility. It is true that all of the other metals except rhodium can exist in the quadrivalent state and in this condition form relatively insoluble salts analogous to ammonium chloroplatinate and isomorphous with it. However, because of the usual course of previous separations, osmium and ruthenium are seldom present with platinum except in very small amounts. Palladium is readily reduced from the quadrivalent to the bivalent state by heating the solution. It is probably true that iridium also is reduced in part, at least, from the quadrivalent state to the tervalent state by heating, especially if the temperature reaches 140–150°C. The ammonium salts of the chloro acids of bivalent palladium and tervalent iridium are much more soluble than ammonium chloroplatinate and not isomorphous with it.

With the possible exception of iridium, therefore, one might expect to eliminate the metals of the platinum group about as rapidly as gold and the base metals, by repeated precipitation of ammonium chloroplatinate. This is not the case. Rhodium, iridium, and palladium display remarkable persistence in contaminating the platinum salt, and rhodium is about as tenacious in this respect as iridium.

Silver may persist through several steps of purification because of the solubility of silver chloride in strong chloride solutions. Part of the dissolved silver chloride is carried down with the precipitate of ammonium chloroplatinate, only to redissolve with the platinum when the sponge is treated with aqua regia. However, experience indicates that silver and gold as well as base metals are usually eliminated before the last traces of platinum metals disappear.

In general, the procedure for preparing pure platinum by repeated precipitation of ammonium chloroplatinate has been as follows: The crude sponge is dissolved in aqua regia in a porcelain dish provided with a cover glass to prevent loss by spraying. For 100 g. of metal, 300 to 350 ml. of hydrochloric acid (sp.gr. 1.18), 75 to 100 ml. of water, and 60 to 70 ml. of nitric acid (sp.gr. 1.42) are used. The temperature is raised rather slowly to avoid too vigorous a reaction. In some cases more aqua regia is required for complete solution. The solution is evaporated fairly rapidly without previous filtration until the temperature reaches 140–150°C., unless the residue becomes pasty before this temperature is reached, in which case the evaporation must be stopped to avoid local overheating. If the sponge contained no large amount of base metal or alkali salt, the solution will be fluid at 150°C. A small amount of water is then added, which causes a lively boiling and the evolution of nitrous fumes. More water is added to cool the solution below 100°C. After digestion for a few minutes, some hydrochloric acid is added and the evaporation repeated.

This whole process can be repeated three or four times in a short while, insuring the elimination of nitrous compounds and no doubt promoting the reduction of quadrivalent iridium to the tervalent state. After the last evaporation water only is added and the solution diluted so as to contain not less than 50 and not more than 100 g. of platinum in 1 liter. It is set aside to allow settling of insoluble matter and then decanted or filtered from any residue. The residue may contain undissolved iridium or rhodium as well as silver chloride, silica, and other insoluble matter.

The solution is heated nearly to boiling and treated with a 20 per cent solution of ammonium chloride, using 55 to 60 g. of the salt for each 100 g. of platinum and adding enough in excess so that the whole solution will contain 3 to 5 per cent of the salt. A moderate excess of ammonium chloride is desirable to decrease the solubility of the platinum salt, but a large excess increases the degree of contamination too greatly. The solution is cooled rapidly, and the platinum salt immediately filtered off and drained by suction. If the solution is allowed to stand, a small amount of ammonium chloroplatinate of lower purity will separate and thus contaminate the main precipitate. The salt is drained well, returned to the dish, and thoroughly mixed with a wash solution containing 20 per cent of ammonium chloride. After draining the salt, this whole process of washing is repeated once more. The salt is dried and ignited to sponge. The filtrates and washings are evaporated to recover most of the residual platinum in a second crop of ammonium chloroplatinate, less pure than the first, and for the recovery of other precious metals by precipitation with zinc.

In dealing with very pure platinum, suitable precautions must be taken with the containers and the manner of heating, to avoid contamination of the metal during ignition of the salt. In the laboratory of the National Bureau of Standards ordinary porcelain ware has often been used, as well as some special procelain with a glaze of high softening point. Metal vapors from windings in electrically heated furnaces are to be avoided, if very pure sponge is desired. This can be done by using a glazed muffle or other glazed lining between the heating element and the vessel containing the sponge. When possible, it is desirable to bring about the decomposition of the salt in a reducing atmosphere, preferably hydrogen. If ammonium chloroplatinate is ignited in the air, there is always some loss of platinum, probably caused by the volatilization of platinous chloride. After the salt is decomposed, the ignition is continued in air. If it is desired simply to prepare the sponge for another step in the process of purification, it is not necessary to exceed a temperature of 500–600°C. A higher temperature causes the sponge to shrink, which makes it more suitable for melting.

(b) By first removing impurities by collective precipitation

Although reprecipitation with ammonium chloride provides an entirely satisfactory way of preparing platinum in any degree of purity, the method is tedious and time-consuming. By first removing impurities by collective precipitation of hydrated oxides, considerable time can be saved.

By the use of this method of removing impurities, and subsequent precipitation of the platinum once with ammonium chloride and ignition to sponge, platinum of an estimated purity of 99.99 per cent was prepared from scrap platinum containing 5 to 10 per cent of impurities, principally platinum metals. From scrap containing 99 per cent of platinum, metal estimated to be 99.995 per cent pure was obtained. Under less favorable conditions metal estimated to be from 99.95 to 99.97 per cent pure was obtained from Colombian grain platinum containing about 84 per cent of platinum, 3 per cent of gold, 8 per cent of iron, 3 per cent of iridium, palladium, and rhodium combined, and 1 per cent of silver and copper. Most of the gold had been removed first by a preliminary treatment of the ore with cold aqua regia.

The procedure used is as follows: The solution of impure platinum in aqua regia is evaporated once or twice to eliminate nitric acid in the manner previously described. Enough sodium chloride is added to form sodium chloroplatinate and similar salts of the other metals. The solution is evaporated and the residue thoroughly dried to remove as much of the hydrochloric acid as possible. The residue is dissolved in water and the solution diluted so as to contain about 50 g. of platinum in 1 liter. If gold is thought to be present, ferrous sulfate solution is added in small portions until no further precipitation of gold occurs. The solution is decanted from the residue and heated nearly to boiling, after which sodium bicarbonate is added in small portions to neutralize most of the remaining hydrochloric acid. When the solution is nearly neutral, as may be judged by diminishing effervescence, 10 to 12 g. of sodium bromate for each 100 g. of platinum is added, only a little being added at first to determine whether the solution is nearly enough neutral not to decompose the bromate. If bromine is evolved, more sodium bicarbonate is added until the addition of a little sodium bromate causes no further evolution of bromine. The remaining sodium bromate is then added, and the addition of small portions of sodium bicarbonate is continued until the solution just turns sensitive litmus paper blue. The solution is now brought rapidly to boiling and again tested with litmus paper. If it is acid, a little more sodium bicarbonate is added and the solution is then boiled for 3 to 5 min. It is finally tested once more; if it is not alkaline, another small portion of sodium bicarbonate is added and the boiling continued for a minute. The solution is then cooled rapidly in running water. Normally, the precipitate of hydrated oxides settles rapidly, after which the supernatant solution is siphoned off and passed through a filter to collect suspended precipitate.

The solution containing the platinum is digested with hydrochloric acid to decompose the bromate, and the platinum is precipitated with ammonium chloride. The ammonium chloroplatinate precipitated from this solution will carry down considerable sodium chloride, most of which may be removed by leaching with water after the salt has been ignited to sponge. The precipitate, which consists of the hydrated oxides of palladium, rhodium, iridium, and base metals, obtained by the treatment with sodium bicarbonate, is dissolved in hydrochloric acid. The solution is worked over for precious metals. More or less platinum will be present, depending on the size of the precipitate and other conditions, but the amount should rarely exceed 5 per cent of the platinum in the solution.

2. Palladium

Palladium is perhaps the most simply purified metal of the group. As previously mentioned, commercial refining practice makes use of the property possessed by dichlorodiamminepalladium, $[Pd(NH_3)_2Cl_2]$, of dissolving in ammonium hydroxide and by reprecipitating when the solution is acidified with hydrochloric acid. With the necessary filtrations, and by repeating the operation, palladium of a high degree of purity can be prepared.

If, however, palladium of the very highest purity is to be prepared, it is probably desirable to follow the several reprecipitations of dichlorodiamminepalladium by one or more precipitations as ammonium chloropalladate, $(NH_4)_2[PdCl_6]$. If this is to be done, the yellow dichlorodiamminepalladium is dried and ignited to sponge in an atmosphere of hydrogen. The sponge is dissolved in aqua regia and the excess of acid eliminated by evaporation. The residue is diluted and filtered to remove silica or other insoluble matter which may have been introduced by the previous operations involving ammoniacal solutions. The volume of the solution is adjusted to contain 100 g. or more of palladium in 1 liter. An equal volume of saturated ammonium chloride solution and one-third as much nitric acid (sp.gr. 1.42) are added, and the whole solution is then digested in a covered dish on the steam bath until the palladium is precipitated as the crystalline red salt, ammonium chloropalladate. The precipitation can be made so nearly complete as to leave a mother liquor which is almost colorless. The salt is filtered off on a Büchner funnel and washed with a 20 per cent solution of ammonium chloride. If a second precipitation is to be made, the salt is ignited to sponge and redissolved in aqua regia. As was previously mentioned, this method of purification, that is, by repeated precipitation with ammonium chloride, aids in the removal of base-metal impurities, particularly those which remain dissolved in an ammoniacal solution, but it does not tend to eliminate the other platinum metals rapidly.

3. Rhodium

Of the six platinum metals, rhodium and iridium are the most difficult to prepare in the highest degree of purity. The following description is that of the procedure used to prepare rhodium for measurement of its freezing point (757), and to a considerable extent it supersedes that given in an earlier publication (747). Since this earlier publication further experience has shown that the repeated precipitation of ammonium rhodium nitrite, although very effective for removing other impurities, is not satisfactory for removing more than very small amounts of iridium. In order to reduce the iridium content of the rhodium to an amount suitable for the application of the nitrite process, the following method was used for dissolving the rhodium.

The impure rhodium was mixed with about twenty parts of lead, and the mixture was fused in a graphite crucible at about 1000°C. for half an hour. Although it might sometimes be disadvantageous to add lead to rhodium, because of the difficulty of eliminating all of it in the subsequent process of purification, it is usually of no consequence, because lead is very often an impurity in rhodium. The resulting alloy was treated with nitric acid to dissolve most of the lead. In this treatment a little rhodium dissolved, but most of it was left as a finely divided alloy with lead. This alloy was vigorously attacked, first with concentrated hydrochloric acid, and then with aqua regia, leaving finally a residue which contained nearly all of the iridium, together with a small portion of the rhodium.

Most of the lead was precipitated from the acid solutions with sulfuric acid, added in slight excess. The filtrates from the lead sulfate were combined and evaporated to a small volume to expel most of the free acids and to obtain a second precipitate of lead sulfate. The filtrate from this precipitate was treated with a sufficient amount of a solution of sodium nitrite to neutralize the remaining free acid and to convert the rhodium chloride into sodium rhodium nitrite, $Na_3[Rh(NO_2)_6]$. The solution was boiled to complete the conversion to nitrite. To this solution, which contained about 50 g. of rhodium in 1 liter, was added about 30 g. of sodium sulfide crystals for each 100 g. of rhodium. This was done to precipitate certain base-metal impurities, such as copper and lead. Some of the platinum-metal impurities, especially palladium, are partially precipitated by this treatment, but very little of the rhodium is lost. After standing overnight, the sulfide precipitate was filtered off and the solution boiled to consume any remaining sodium sulfide by its reaction with platinum-metal impurities or with the rhodium itself. After removal of the second small precipitate of sulfides, the solution was cooled to about 15°C. and treated with a solution of ammonium chloride to precipitate a salt which has generally been regarded as $(NH_4)_3[Rh(NO_2)_6]$ but which may be a mixed sodium and ammonium rhodium nitrite. About 200 g. of ammonium chloride was used for each 100 g. of rhodium. This proportion includes a small excess of ammonium chloride, which decreases the solubility of the double salt.

After filtering and washing the salt, it was decomposed with hydrochloric acid diluted with three or four volumes of water. The chloride solution was then evaporated to expel most of the hydrochloric acid and the cycle of operations with sodium nitrite, sodium sulfide, and ammonium chloride repeated six times. The quantity of sodium sulfide used was decreased each time, and the sulfide precipitates were examined chemically for lead. Lead was not detected after the fourth precipitation. At this stage a solution of sodium nitrite which had been treated to remove traces of base metals was substituted for the ordinary reagent.

Spectrochemical examination of the rhodium from the fifth precipitation failed to disclose the presence of any other platinum metals, but indicated a trace of lead. Lead was not found in the metal from the sixth precipitation. The salt obtained by the seventh precipitation was converted into a chloride solution, by means of hydrochloric acid, and ammonium chloride was added in slight excess of the amount equivalent to $(NH_4)_3[RhCl_6]$. The ammonium chlororhodate was then precipitated from this solution, which contained about 100 g. of rhodium in 1 liter, by adding 1.5 times its volume of 95 per cent alcohol. The salt was washed with alcohol, dissolved in water, and reprecipitated by means of alcohol from a somewhat more dilute solution. The salt thus prepared contained, after drying, 30.7 per cent of rhodium.

The salt was ignited in a porcelain container in a resistance furnace in such a way as to prevent contamination with metal vapors from the winding. The residue was reduced to rhodium sponge by ignition in hydrogen, and the sponge digested with water to extract a small amount of alkali salts.

Since the work described above was done, much has been learned about the conditions under which various base metals, including lead, can be precipitated hydrolytically from the nitrite solutions of the platinum metals. In view of this the repeated treatment with sodium sulfide probably could be greatly simplified, if not eliminated.

4. Iridium

The purification of iridium is attended by unusual difficulties. The literature on iridium does not include methods which can be depended upon for the complete elimination of impurities, even though they may be satisfactory for preparing metal of commercial purity.

The following discussion was written concerning the method used to prepare iridium for the measurement of its freezing point (754). Like the description for the preparation of pure rhodium, this for iridium modifies somewhat the one given in an earlier publication (747) of the National Bureau of Standards.

All the base metals ordinarily associated with iridium, as well as silver, gold, and probably palladium, can be removed by precipitating the iridium several times as ammonium chloroiridate, $(NH_4)_2[IrCl_6]$, provided proper precautions are taken. Platinum and ruthenium, on the other hand, cannot be separated from iridium in this way because they form chloro salts of the same order of solubility as the iridium salt. Even rhodium, which does not form an analogous, slightly soluble chloro salt, will contaminate the iridium compound with the utmost persistence, so that it is wholly impracticable, if not impossible, to get rid of rhodium in this way. No difficulty is experienced with osmium, which, although it forms a chloro salt similar to that of iridium, is volatilized as the tetroxide when the solution is digested repeatedly with nitric acid or aqua regia, in the usual refining process.

When iridium is precipitated as ammonium iridium nitrite, platinum and ruthenium concentrate rapidly in the mother liquors and could probably be completely eliminated by several precipitations of that salt. This procedure can also be adapted to the separation of most of the base metals. However, in this instance it is rhodium which forms an analogous salt, somewhat less soluble than the iridium compound. Hence, rhodium could be eliminated only by a long-continued process of fractional precipitation, which is not very suitable when only a limited amount of material is available, and which in any case is not favorable to the purification of the more soluble of the two salts. Such a method would be better for freeing rhodium of iridium than *vice versa.*

Up to the present time no slightly soluble, easily handled compound of iridium has been thought of which can be repeatedly precipitated and thereby effect the complete removal of rhodium. The earlier work indicated that ruthenium could be eliminated by fractional precipitation with hydrogen sulfide, but that the yield of iridium was not very favorable. Later work has shown that this treatment also gets rid of rhodium and platinum. The poor yield (sometimes only 50 per cent of fairly pure starting material) is offset by the simplicity of the operation and the fact that all three of the most persistent impurities are eliminated together.

Briefly, the procedure followed for the preparation of pure iridium consisted in saturating the acidified chloride solution (50 g. of metal and 50 ml. of concentrated hydrochloric acid in 1 liter was found to give satisfactory conditions of concentration) with hydrogen sulfide at room temperature and keeping it saturated for a week or longer, during which time platinum, rhodium, ruthenium, etc. slowly precipitated, together with a portion of the iridium. The precipitation was stopped when spectrochemical examination of the iridium obtained from the filtered solutions showed no trace of other platinum metals. Foreign metals which were not completely removed by hydrogen sulfide at the prevailing acidity were then eliminated by repeated precipitation of ammonium chloroiridate, sometimes combined with one or more precipitations of ammonium iridium nitrite.

Later work has shown that the yield of iridium, that is, the amount left unprecipitated by the hydrogen sulfide, was greater when a more concentrated solution of iridium was used and its acidity more carefully controlled. When the chloroiridic acid was converted to its sodium salt, and the resulting solution made to contain 100 g. of iridium and 35 ml. of concentrated hydrochloric acid in 1 liter, a yield of over 80 per cent was obtained. Spectrochemical examination of iridium prepared in this way disclosed no platinum-metal impurity except a trace of rhodium. To obtain a good yield, it is necessary to eliminate most of the platinum metals by other methods, before applying the fractional precipitation with hydrogen sulfide.

5. *Osmium*

Osmium, isolated by distillation as osmium tetroxide and absorbed in sodium hydroxide, may be recovered in a number of ways. The commercial procedure is to form osmyltetrammine chloride, which is ignited in hydrogen to metal.

A simple way is to precipitate hydrated osmium dioxide hydrolytically by neutralizing the solution with hydrochloric or sulfuric acid. By whatever method the osmium is recovered, the reduced metal obtained serves as the starting point for the preparation of pure osmium.

The procedure for preparing pure metal is as follows: Metallic osmium, recovered by any of the methods just mentioned, is heated in boats in a hard-glass tube, using an electric furnace for the purpose. Half of the glass combustion tube is bent downward at an angle of 45° and the end of the tube just submerged in 6 N hydrochloric acid contained in an Erlenmeyer flask. A slow current of oxygen is passed through the tube. At about 220–230°C. a vigorous reaction occurs, accompanied by a rapid absorption of oxygen and a progressive glowing of the metal. The resulting product is a black powder of greater bulk than the metal, and is probably osmium dioxide. At this stage it is necessary to supply oxygen rapidly to avoid a diminished pressure in the tube.

After this reaction subsides, the temperature is raised gradually, whereupon the material in the boats is quietly oxidized to osmium tetroxide. The latter compound condenses to a solid in the cool portion of the tube. When oxidation of the material in the boats is complete, the solidified tetroxide in the tube is loosened by gentle warming and dropped into the flask. It is then quickly transferred to a flask fitted to a reflux condenser by a ground-glass joint. The top of the condenser is fitted with a trap containing sodium hydroxide.

In the reaction flask the osmium tetroxide is gradually converted to chloroosmic acid, $H_2[OsCl_6]$, if hydrochloric acid is used, or to bromoösmic acid, $H_2[OsBr_6]$, if hydrobromic acid is used. A small amount of alcohol aids the reaction with hydrochloric acid, but it is not actually necessary with hydrobromic acid. The flask is warmed gently, and the temperature raised gradually to that of incipient boiling during a period of 3 hr. In the case of hydrochloric acid the reaction may be regarded as complete when the color of the solution changes to a clear transparent red, characteristic of $H_2[OsCl_6]$, and no droplets of condensing tetroxide are observed or the odor of tetroxide detected. At least twice the theoretical amount of hydrochloric acid required to form $H_2[OsCl_6]$ should be used. The reaction with hydrobromic acid is much more rapid than that with hydrochloric acid, and it is to be preferred if large amounts of osmium are being handled.

Solutions of chloroösmic acid are stable and do not decompose or lose osmium on evaporation if the acid concentration is at least 2.8 N. Ammonium chloride precipitates brick-red ammonium chloroösmate, $(NH_4)_2[OsCl_6]$, from solutions of the chloro acid; and ammonium bromide precipitates brownish black ammonium bromoösmate, $(NH_4)_2[OsBr_6]$, from solutions of the bromo acid. Ignition of either of these salts in hydrogen yields osmium sponge, which is cooled in an inert gas such as nitrogen or carbon dioxide.

If metal of the very highest purity is desired, as for the determination of atomic weights, the cycle of operations is repeated, using specially prepared reagents.

6. Ruthenium

Ruthenium, isolated by distillation as ruthenium tetroxide, is absorbed in hydrochloric acid diluted with four volumes of water. The solution is evaporated on the steam bath to eliminate the excess of hydrochloric acid. The addition of ammonium chloride to a filtered concentrated solution of the chloro acid of ruthenium precipitates a salt, probably $(NH_4)_2[RuCl_5OH]$ or $(NH_4)_2[RuCl_6]$. This salt is filtered on a Büchner funnel and washed with a 20 per cent solution of ammonium chloride. Reduction of the salt in hydrogen produces metallic ruthenium.

VI. Analysis of Platiniferous Materials

To appreciate the advances which have been made during the past twenty years in perfecting methods for analyzing platiniferous materials, it is well first to examine the state of the analytical chemistry of the precious metals at the beginning of the World War.

A. TRADITIONAL METHODS

Holtz (791), after considering the methods (782, 786, 788, 789, 798) which had been proposed for the analysis of native grain platinum and for platinum alloys, schematic diagrams of which are reproduced in the book published by Duparc and Tikonowitsch (763), attempted to incorporate their various desirable features, together with some of his own devices, into a procedure which he used to analyze native platinum. Holtz' modifications, however, added little to the solution of the riddle of analyzing crude platinum. Two of the methods just cited do deserve attention: namely, that of Deville and Stas for the analysis of platinum alloys, and that of Leidié, which has recently been developed into a procedure for analyzing dental gold alloys (760).

An important contribution made at Geneva was the application by Wunder and Thüringer (812) of Chugaev's dimethylglyoxime to the separation and determination of palladium. The precipitation of palladium by dimethylglyoxime deserves a place in the front rank of analytical reactions. Its very excellence serves to show by contrast how great are the shortcomings of some of the traditional analytical methods for the platinum group.

1. Separation of platinum, palladium, rhodium, and iridium from one another by ammonium chloride

The most common operation in the analysis of platiniferous material has been the precipitation of platinum as ammonium chloroplatinate. This reaction has been generally used to separate platinum from rhodium and palladium and, in some schemes of analysis, from iridium after reducing this metal to the tervalent state. The convenience of this method of separation is so great that the analyst has been prone to ignore its inherent errors. One type of error results from the persistent contamination of the platinum salt by rhodium and iridium, even though these metals be tervalent, and, to a less extent, by palladium. The other error occurs because ammonium chloroplatinate is appreciably soluble.

It is true that the solubility of the platinum salt can be reduced to an amount which may be negligible in some analytical procedures, by adding a large excess of ammonium chloride and digesting the solution. These conditions, however, greatly increase the contamination of the salt by the other platinum metals. It is not at all unusual, for example, if a small amount of rhodium is present, for the familiar orange-yellow compound to turn bright green as the digestion proceeds. The solubility of the platinum salt also deters the careful analyst from reprecipitating it one or more times to purify it. When this is done, the increase in analytical accuracy resulting from the improved separation from the related metals is offset by loss of platinum. The practical consequence is that a determination of platinum which is based on its separation from the other platinum metals by precipitation with ammonium chloride or potassium chloride can be accurate only by the accident of compensating errors.

The shortcomings of the precipitation of ammonium chloroplatinate for analytical purposes were well recognized by such early workers as Deville and Stas. In their excellent work on the analysis of the platinum–iridium alloy used to fabricate the International Prototype Meter, these authors discussed at length the incomplete precipitation of ammonium chloroplatinate and its contamination by other metals, especially rhodium. They showed that the degree of contamination varies with the mode of precipitation. Under the best conditions of separation, the platinum obtained in an analysis of an alloy containing 0.65 per cent of rhodium still contained 0.2 per cent of rhodium. Moreover, a considerable amount of platinum remained in the mother liquor and was recovered with the major part of the rhodium. They quite frankly regarded precipitation with ammonium chloride as a preliminary separation. A further separation was obtained by extracting the rhodium from two or three fractions, obtained by means of ammonium chloride, with molten potassium pyrosulfate. This is at best a laborious operation which must be repeated several times. Furthermore, a portion of the platinum dissolves in the pyrosulfate and not all of the rhodium can be extracted. The method offers a closer approximation to an accurate separation of rhodium from platinum than does the procedure with ammonium chloride alone and reflects credit on the efforts of its authors to determine the actual rhodium content of the material they examined. Nevertheless, it is much too tedious for routine use and not satisfactory when a high degree of accuracy is necessary.

The separation of iridium from platinum by means of ammonium chloride has the same shortcomings as the separation of rhodium from platinum. In addition, there is the difficulty of reducing all of the iridium to the tervalent state before precipitating the ammonium chloroplatinate. Too vigorous reduction of the mixed chlorides may result in a partial reduction of platinum to the bivalent condition. Frequently, the effort of the analyst has been directed toward keeping both the iridium and platinum in the quadrivalent state and precipitating the two together with ammonium chloride, in the hope of first separating them from rhodium and palladium. The subsequent separation of the iridium and platinum from each other was based on igniting the mixed salt to sponge and extracting the platinum with diluted aqua regia. Such an extraction cannot yield accurate analytical results, except by the accident of compensating errors, because iridium sponge is not wholly insoluble in aqua regia and because platinum is not completely extractable. Experience also shows that it is even more difficult to get approximately complete precipitation of ammonium chloroiridate than of ammonium chloroplatinate. Furthermore, rhodium is entrained by the iridium salt even more persistently than by the platinum salt. Palladium appears to be more easily separated from platinum by ammonium chloride than is rhodium or iridium. Fortunately, the analyst is now in possession of the organic reagent dimethylglyoxime, and has no further worries with palladium.

The only truly quantitative separation of iridium from platinum which had been developed prior to 1914 is that discovered by Deville and Stas (789) and used by them for the determination of iridium in alloys from which the Prototype Meter was fabricated. In this method the platinum–iridium alloy is melted with about ten times its weight of lead, thus producing alloys of lead and platinum which are soluble in acids, and crystalline iridium which is virtually insoluble in aqua regia. A study of the method at the National Bureau of Standards (742, 743) confirmed its accuracy and led to certain modifications which increase the ease and speed of operation. The method is an excellent one for the routine analysis of platinum alloys which contain no iron or ruthenium (or osmium). In the lead fusion, ruthenium alloys itself quantitatively with the iridium, and iron nearly so. The subsequent removal of ruthenium and iron, to obtain a correct determination of iridium, is laborious. As a method for determining iridium only, in an alloy containing iridium, platinum, rhodium, palladium, gold, and copper, for instance, it stands as a tribute to the ingenuity of its authors.

B. METHODS OF EFFECTING SOLUTION OF PLATINIFEROUS MATERIALS

Relatively few types of reactions are used to effect solution of platiniferous materials. Material which is insoluble in aqua regia, such as osmiridium, metallic iridium, and metallic rhodium, is usually rendered soluble by means of fusion with alkaline oxidizing fluxes, followed by treatment with hydrochloric acid. Mixtures of sodium hydroxide and sodium nitrate or of sodium hydroxide and sodium peroxide are frequently employed. Barium peroxide alone is sometimes used. In these operations it is necessary to use vessels of gold, silver, nickel, or iron. Rhodium is conveniently converted to a soluble form by heating its mixture with sodium chloride in an atmosphere of chlorine.

A method recently developed by Wichers, Schlecht, and Gordon (761, 762) at the National Bureau of Standards deserves particular mention, because it solves one of the most difficult problems of the platinum analyst. They found that refractory platiniferous material could be brought completely into solution by heating it in contact with hydrochloric acid which contains a small amount of a suitable oxidizing agent, in a sealed glass tube at an elevated temperature. The rate of attack varies greatly with the composition of the acid mixture as well as with the temperature. A mixture of twenty volumes of concentrated hydrochloric acid with one volume of fuming nitric acid, or an equivalent amount of sodium chlorate, perchloric acid, or chlorine, is satisfactory. Such a mixture at a temperature of about 300°C. will dissolve osmiridium and even metallic iridium at a fairly rapid rate. Leaving the tubes in a controlled oven for 24 hr. is sufficient for an average specimen of osmiridium, but large grains or exceptionally refractory specimens may take longer. About 20 ml. of the acid mixture is used for 1 g. of metal. If the samples are as small as 100 mg., heavy-walled glass tubes of 4-mm. bore and about 20 cm. long, half filled with acid, can be heated safely to 300°C. without much danger of bursting. Larger tubes are heated in a steel bomb into which a weighed amount of solid carbon dioxide is put to provide the proper compensating pressure. Pressures within the glass tubes are estimated at 3500 to 4000 pounds per square inch at 300°C.

When the solution of the sample is complete, the tube is chilled in a bath cooled with solid carbon dioxide before it is cut open. This serves to reduce any excess pressure within the tube and to prevent the escape of volatile substances, such as osmium tetroxide. The opened tube is then inverted in a solution of hydrochloric acid containing sulfur dioxide, and allowed to come to room temperature. This effectively prevents loss of osmium tetroxide.

In general the method is advantageous because any type of platiniferous material can be brought into chloride solution without loss of any constituent and without introduction of large amounts of alkali salts. For details concerning the optimum conditions of attack of various materials, a forthcoming paper (762) in the *Journal of Research of the National Bureau of Standards* should be consulted.

C. METHODS OF SEPARATION BASED ON HYDROLYTIC PRECIPITATION

The formation of insoluble hydroxides of the platinum metals is not a newly observed phenomenon. A century ago milk of lime was added to solutions of native platinum in the process of refining at the Russian Mint. Claus (784), the discoverer of ruthenium, did point out that the elimination of impurities by this method was never complete.

In 1914 Mylius and Mazzucchelli (803) used a solution of sodium bicarbonate in bromine water for the collective precipitation of impurities in the approximate analysis of commercial platinum. They did not, however, obtain quite complete separation of the impurities. Somewhat later, Wichers (745), modifying the method of Mylius and Mazzucchelli, developed a hydrolytic procedure for separating rhodium from platinum, and made observations on the behavior of the other platinum metals.

In a series of experimental researches Gilchrist (748, 750, 752, 755, 756) developed a complete system of analysis for the platinum group, in which the method of hydrolytic precipitation was utilized. A discussion of this new method is given in the proceedings of the Ninth International Congress of Pure and Applied Chemistry (758), and of the analytical procedure in the *Journal of the American Chemical Society* (759).

These researches revealed that there were some ranges of hydrogen-ion concentration within which the members of the platinum group, with the exception of platinum itself, are completely precipitated by hydrolysis, when in the form of their chloro acids. For osmium the range appears to be about pH 1.5 to 6, with optimum conditions at pH 4; for iridium, pH 4 to 6; while for rhodium and palladium an alkalinity equivalent to pH 6 is the minimum that will insure complete precipitation. For ruthenium the conditions appear to be such that little variation from pH 6 is permissible. Palladium, rhodium, and iridium are most advantageously precipitated in the presence of sodium bromate, and in the complete analytical procedure it is recommended that the neutralization be finally carried to pH 8 to make certain that palladium and rhodium are completely precipitated. This alkalinity has no disturbing effect on the iridium precipitate.

Not all reagents which can furnish the necessary hydroxyl-ion concentration are suitable as neutralizing agents, because some of them,—for example, nitrite, phosphate, and ammonium hydroxide,—convert the chloro compounds of the platinum metals into other types of compounds, rather than into insoluble hydroxides.

The control of the acidity or alkalinity at which the platinum-metal hydroxides are to be precipitated cannot usually be attained by means of an indicator added directly to the solution. Solutions of the platinum metals are highly colored, and the precipitates which form obscure observation of the indicator. Furthermore some of the reagents, such as bromate, destroy the indicators. Nevertheless, it is possible to utilize indicators in a very simple manner. The operation of testing is performed by lifting the stirring rod above the level of the solution and adding a drop of the indicator to the drop which has clung to the end of the rod. The stirring rod is then replaced in the solution, with no loss of material. This method of testing is not that of the usual "outside indicator". The end point determined in this way is practically identical with that determined by adding the indicator directly to the main body of a solution.

The indicators which have proved to be the most useful in controlling hydrolytic precipitations are the sulfonphthalein indicators, in the form of their monosodium salts, at a concentration of 0.01 per cent. These indicators are: thymol blue, which changes from red to orange at about pH 1.5, in the direction from acid to alkaline, and from yellow to blue at about pH 10; brom phenol blue, yellow to blue at pH 4; brom cresol green, yellow to blue at pH 4.7; chlorphenol red, yellow to red at pH 6; brom cresol purple, yellow to blue at pH 6.3; brom thymol blue, yellow to blue at pH 7; cresol red, yellow to pink at about pH 8; and xylenol blue, yellow to blue at an alkalinity slightly greater than pH 8.

D. SEPARATION OF THE PLATINUM METALS FROM ONE ANOTHER

1. Separation of palladium, rhodium, and iridium from platinum, by hydrolysis

The superiority of the hydrolytic method in effecting the separation of platinum from palladium, rhodium, and iridium lies in the fact that the separations are clean-cut, simple, and quantitative. Palladium, rhodium, and iridium, either singly or collectively, can be separated from platinum. If the separation is effected in the presence of bromate, the hydroxides settle well, are readily filtered, and contain so little platinum that the separation obtained by a single precipitation is superior to that obtained by many commonly used procedures, and needs to be repeated only once to attain strictly quantitative accuracy.

Oxidation of palladium, rhodium, and iridium is readily accomplished by adding a small amount of sodium bromate to the hot, slightly acidified solution prior to neutralization. The addition of bromate has the further advantage that it retards the reaction of the chloroplatinate radical with hydroxyl ions. The way in which it does so is as yet unexplained, but the effect is unmistakable. It is not really necessary, however, to add bromate for the purpose of retarding the hydrolysis of the chloroplatinate radical, because this radical hydrolyzes so slowly at pH 6 and at the concentrations of platinum usually handled in analytical work that there is no interference. In any case, the first stages of the hydrolysis of chloroplatinate do not result in the formation of insoluble compounds. The essential purpose of the bromate is, of course, to insure the oxidation of palladium, rhodium, and iridium to a state of valency higher than that at which they normally exist.

Not long after the accidental death of Ludwig Moser of the Technische Hochschule at Vienna, two of his students, Hackhofer and Graber, reported on the separation of iridium (400) from platinum, and of rhodium (401) from platinum, by a hydrolytic procedure in which the alkalinity of the solution is fixed by the reaction between bromate and bromide ions. This reaction, however, appears to come to equilibrium so slowly that prolonged boiling and digestion are required to complete the precipitation. In the case of iridium, particularly, the hydrolytic product which is formed is very difficultly soluble. In their procedures, these authors make no provision for repeated precipitation to eliminate platinum completely.

2. Isolation of palladium

Wunder and Thüringer, in precipitating palladium with dimethylglyoxime in the presence of platinum in a hot solution, encountered difficulty in effecting the separation. The cause of this difficulty lies in the reduction of some of the platinum from the quadrivalent to the bivalent state. Like palladium, which is bivalent, bivalent platinum also forms the same kind of inner complex salt with dimethylglyoxime. To avoid this difficulty, Wunder and Thüringer, in their procedure (812) for the isolation of palladium in the analysis of native platinum, recommend that the platinum and iridium be removed first, by precipitation with ammonium chloride. The palladium (together with gold) is then precipitated from the boiling filtrate by adding dimethylglyoxime.

It remained for Davis (712) to point out that the coprecipitation of platinum which occurs in a hot solution can be avoided by operating at room temperature, and that the results thus obtained are very satisfactory if the palladium is reprecipitated, even though the original ratio of platinum to palladium happens to be large. Swanger (746), in his development of a procedure for the analysis of dental gold alloys, confirmed the experience of Davis.

The precipitation of palladium in the presence of platinum can be made and is recommended in certain instances, provided it is performed in cold solution and the precipitate is not allowed to remain too long before being removed by filtration. Swanger performed the second precipitation of palladium, in its separation from platinum, by decomposing the glyoxime precipitate first obtained with nitric acid or aqua regia, diluting the solution, and adding more glyoxime. If this is done, it should be borne in mind that a small amount of palladium may remain in solution. It is not apparent why this should occur unless, perhaps, a small amount of the palladium exists as a nitroso compound which does not react with the glyoxime.

The ideal conditions for the application of dimethylglyoxime to the isolation of palladium, in the analysis of platiniferous materials, exist when the platinum has first been completely removed. The hydrolytic method of treatment accomplishes the removal of platinum simply and efficiently. With platinum completely eliminated, the problem of isolating palladium with dimethylglyoxime is greatly simplified. With the amounts of palladium, rhodium, and iridium ordinarily handled analytically, a single precipitation of palladium by dimethylglyoxime separates this metal from rhodium and iridium without contamination. The precipitation is best made in a solution of these three metals as chlorides or sulfates, to which forms the hydrated oxides are readily converted. If the amount of iridium is large, and the iridium has been converted to the blue form of its sulfate by fuming with sulfuric acid to which nitric acid has been added, some trouble may be encountered. It was observed that under such circumstances the glyoxime precipitate seemed finely divided and a colloidal substance tended to pass through the filter. If, however, the iridium is entirely in the tervalent state, as is also the rhodium under all conditions, no interference occurs. A theoretical explanation of the reason why rhodium and iridium do not contaminate the precipitate of palladium with dimethylglyoxime is considered in Section VIII.

3. Separation of rhodium and iridium from each other

The separation of rhodium from iridium has long been one of the most difficult of the analytical problems of the platinum group of metals. Berzelius (782), in a general scheme for the analysis of crude platinum, used molten potassium bisulfate to separate these two metals from each other. This method is unsatisfactory because of the incomplete removal of rhodium and the partial solution of iridium. The separation of rhodium from iridium by ammonium chloride has already been discussed.

As previously mentioned, Deville and Stas (789) had discovered a reaction, involving fusion with lead, whereby iridium could be isolated, and, under certain restrictions, a method based on this reaction effects the quantitative separation of iridium from rhodium. The recovery and isolation of rhodium, however, are another matter. Wöhler and Metz (263) in 1925 substituted bismuth for lead in the procedure of Deville and Stas, as did also Karpov (204) in 1928. More recently it was found possible to effect a strictly quantitative separation of these two metals from each other, and to recover each one for determination. The method (752) by which this was accomplished had its origin in the observation by Wada and Nakazono (682) in 1923 that rhodium is precipitated by the reducing action of titanous sulfate while iridium is not, if the chloride solution of each metal is treated separately. The procedure that Wada and Nakazono described for the separation of rhodium from iridium was apparently not intended to be a quantitative one. Its method of presentation is entirely that of a qualitative procedure. No provision is made for dissolving the precipitated metallic rhodium, in order that it can be reprecipitated to free it of iridium which, under the conditions of their treatment, is partially precipitated.

The successful development of Wada and Nakazono's idea came about through the ability to redissolve the metallic rhodium in boiling sulfuric acid; thus the rhodium could be reprecipitated. It was found that less contamination of the rhodium by iridium occurred if the precipitations were made in a solution containing the two metals as sulfates. Since the second precipitation had to be made in sulfate solution, there was no reason why the first should not be done so too. With the quantities of rhodium and iridium usually handled analytically, two precipitations of the rhodium as metal suffice to effect quantitative separation. Since a 20 per cent solution of titanous chloride can be purchased, this reagent is recommended.

When the operation is over, the analyst is confronted with the problem of removing the considerable quantity of titanium which has been added. Fortunately, the organic reagent, the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N(NO)ONH_4$, ordinarily referred to as cupferron, precipitates quadrivalent titanium in either hydrochloric or sulfuric acid solution. Cupferron also acts as a scavenger. It precipitates a number of other elements beside titanium, notably iron. The iridium is finally recovered by hydrolytic precipitation of its hydrated dioxide.

Karpov and Fedorova (205) in 1933 proposed a method for the separation of rhodium from iridium in which a solution of these metals in strong hydrochloric acid is treated in the cold with mercuric chloride and vanadium dichloride, VCl_2. According to the authors the iridium is reduced to the tervalent state, while the rhodium is reduced to metal and forms an amalgam. They claim that unless the rhodium forms an amalgam it is difficult to redissolve it, and since iridium usually contaminates the precipitate, reprecipitation is necessary. The rhodium amalgam is dissolved in aqua regia, the solution is evaporated, and the residue is heated to drive off mercuric chloride. The resulting residue is dissolved in hydrochloric acid and the precipitation of rhodium is repeated. A third and final precipitation is made without adding mercuric chloride. The rhodium so obtained is ignited, treated with hydrofluoric acid and with hydrochloric acid to remove traces of silica, iron, and zinc, reduced in hydrogen, and weighed. No provision is made for the separation of iridium from vanadium or for its recovery.

4. Isolation of osmium

Distillation of the tetroxide of osmium, usually from a solution acidified with nitric acid, has been universally used to separate this element from the other platinum metals. Despite the general use of this process, no study seems to have been made of the completeness of the separation or of the best operating conditions until 1931, when an investigation of the separation and determination of osmium (750) was undertaken at the National Bureau of Standards.

In this study it was found that the form in which the osmium exists in solution has a marked effect on the speed with which it is eliminated. If it is in the form which results when an osmium-bearing material is fused with alkaline reagents, such as sodium hydroxide and sodium peroxide or nitrate, it is eliminated completely in about 1 hr. from a boiling solution which contains at least 10 per cent of its volume of free nitric acid of specific gravity 1.4. The same thing is true if the osmium exists as bromoösmate, but if it is in the form of chloroösmate as much as 8 hr. may be required to complete the distillation. In the latter case it is better, if possible, to distil from concentrated sulfuric acid. Under these conditions osmium is quickly separated as the tetroxide. (Strangely enough, on the other hand, if the osmium exists as the bromoösmate it is eliminated very slowly from boiling concentrated sulfuric acid.) The addition of a small amount of nitric acid to the sulfuric acid solution further expedites the elimination of osmium. However, nitric acid should not be added to the sulfuric acid unless ruthenium is known to be absent, since ruthenium tetroxide is slowly formed under these conditions. In the absence of nitric acid ruthenium tetroxide is not formed in the boiling concentrated sulfuric acid, and the separation of osmium from ruthenium, as well as from the other metals, is complete. The separation of osmium is also complete when the osmium tetroxide is distilled from a nitric acid solution (containing little or no sulfuric acid), if the concentration of nitric acid does not exceed about 40 per cent. A complete separation of osmium from the other platinum metals is thus found to be possible by the traditional method, if proper precautions are observed.

5. Isolation of ruthenium

The traditional method for separating ruthenium from the other platinum metals, except osmium, is to saturate an alkaline solution of the metal with chlorine, and to remove by distillation the ruthenium tetroxide thus formed. Everyone familiar with this method knows that the process of adding fresh alkali, saturating with chlorine, and distilling must be repeated several times, if even an approximately complete elimination of ruthenium is to be achieved. The cause of the incomplete elimination of ruthenium in this process probably lies in the entrainment of ruthenium by the precipitates of iridium or other hydroxides which are formed when the alkaline solution of sodium hypochlorite is changed to a nearly neutral solution of sodium chlorate, by heating. It has been observed that the precipitate of iridium which is produced under these conditions catalytically decomposes chlorate and bromate with the production of oxygen.

To avoid the difficulty encountered in eliminating ruthenium from an alkaline solution by means of chlorine, a procedure (755) was developed at the National Bureau of Standards by which ruthenium tetroxide is distilled from a solution sufficiently acid to prevent the precipitation of iridium. It was found that bromic acid, produced by adding sodium bromate to a solution containing about 5 ml. of free sulfuric acid of specific gravity 1.84 in 100 ml., will oxidize ruthenium to its tetroxide and permit its complete removal by distillation. The best conditions obtain if the ruthenium has first been converted to ruthenium sulfate. If the ruthenium exists as the chloride, the distilling operation will require about 4 hr.; if it is in the form of sulfate, only 2 hr. are required. The presence of the other platinum metals in the solution, or even of finely divided platinum which is formed during the conversion of chlororuthenate to ruthenium sulfate by fuming with sulfuric acid, does not interfere with the complete elimination of ruthenium tetroxide. The conversion of the ruthenium to its sulfate, prior to distillation, has the advantage of eliminating chlorides. If present, chlorides appear to cause a trace of ruthenium, probably in the form of the dioxide, to deposit on the glass surface near the top of the distilling flask. This deposit is not readily removed.

6. Recovery and determination of the platinum metals

A very suitable reagent in which to absorb quantitatively osmium tetroxide, and also ruthenium tetroxide, consists of 6 *N* hydrochloric acid which is saturated with sulfur dioxide. This reagent reduces these tetroxides and forms chloroösmic acid and chlororuthenic acid, respectively. From the evaporated solutions, after destruction of sulfito complexes, osmium and ruthenium, respectively, are precipitated as hydrated oxides. That of osmium cannot be caught on filter paper, as are the precipitates of the other five platinum metals, and ignited in air. It is best caught in a platinum filtering crucible which has a filtering pad of platinum sponge, known as a Munroe or Neubauer crucible. The precipitate is ignited in hydrogen, the hydrogen is displaced by carbon dioxide, and the metallic residue is weighed. Whenever the hydrated oxides of the platinum metals are ignited, either in hydrogen or in air, they have a tendency to deflagrate, which has been attributed to the splitting off of the water of hydration. This tendency to deflagrate is practically eliminated by impregnating the filter and precipitate with ammonium chloride or sulfate before igniting.

The hydrated oxide of ruthenium is ignited in air to anhydrous oxide, and then reduced in hydrogen to metal. The hydrated oxides of iridium and rhodium are treated similarly. However, when rhodium has been separated from iridium by titanous chloride, it is preferable to recover it as sulfide. In this instance the solution of rhodium sulfate must first be converted to one of rhodium chloride, by treating the strong sulfuric acid solution containing the rhodium with strong hydrochloric acid. Rhodium is precipitated easily and completely by hydrogen sulfide from a solution of its chloride, but it is only partially or not at all precipitated from its sulfate. The sulfide of rhodium is ignited in air to an anhydrous oxide, which is in turn reduced to metal in hydrogen.

Platinum is also recovered as sulfide, ignition of which in air yields spongy metal. Unlike rhodium, platinum retains a small but significant amount of sulfur which must be eliminated if high accuracy is desired. The elimination of sulfur is best accomplished by dissolving the spongy platinum and reprecipitating it by reduction with a reagent such as formic acid. It is necessary to adjust the acidity of the solution to a certain range in order to obtain complete precipitation. Whereas formerly it was recommended to use sodium acetate for this purpose, it was found that it is simpler and preferable merely to add sodium hydroxide until the acidity is reduced to that corresponding to the end point of brom phenol blue (pH 4). If the acidity is maintained at this concentration, reduction to metal is complete, the necessity of boiling is eliminated, and the operation can be conducted at the temperature of the steam bath. Furthermore, the reduction can be accomplished in solutions containing appreciable amounts of sodium salts, a condition which is unfavorable to the use of sodium acetate. Thus, the necessity of making a preliminary precipitation with hydrogen sulfide may often be avoided.

Palladium sulfide cannot be ignited to metal. Often the precipitate will fuse to a globule which strong ignition neither in air nor in hydrogen is able to decompose. Palladium, therefore, should never be determined by igniting its sulfide. It is best determined either by weighing its glyoxime compound or by igniting this compound to metal. The residue obtained is an oxide of uncertain composition which can be converted to metal by ignition in carbon dioxide. Common practice has been to reduce the oxide in hydrogen. When this is done, it is necessary to heat the metal briefly in carbon dioxide, to eliminate the hydrogen which it adsorbs. Since the oxide can be decomposed by ignition in carbon dioxide, it is simpler to dispense with the treatment with hydrogen.

E. PROCEDURE FOR THE SYSTEMATIC SEPARATION AND DETERMINATION OF THE PLATINUM METALS

Detailed directions for the systematic separation of the platinum metals from one another and for their recovery and determination are given in the publication by Gilchrist and Wichers (759). As this publication is easily accessible, no description of the procedure is given here.

F. SEPARATION OF THE PLATINUM METALS FROM OTHER ELEMENTS

In the analysis of commercial platiniferous material it becomes necessary to separate the platinum metals from whatever other elements the material contains.

The most complex naturally occurring platiniferous material is native grain platinum. That which is being recovered in Alaska contains, as major constituents, platinum, iridium, iron, gold, osmium; as minor constituents, rhodium, ruthenium, copper, palladium, silver; as small but chemically determinable constituents, chromium, nickel; and in addition, as constituents detected spectrochemically but not analytically, manganese, cobalt, aluminum, titanium, tin, lead, arsenic, silicon, antimony, magnesium, calcium, strontium, and barium.

The quantity of magnesia and silica may vary considerably, depending upon the degree to which the native platinum is cleaned mechanically.

The modern dental gold alloys represent a general type of material which is frequently encountered in platinum analysis. These alloys always contain silver, gold, and copper; they frequently contain palladium, platinum, tin, and zinc; and occasionally they contain iridium, rhodium, nickel, and indium.

The above-named base metals are the ones which are of chief interest to the analyst.

Osmium and ruthenium are usually isolated in the early stages of an analysis, by distilling their respective tetroxides. This early removal is necessary to avoid their loss by reaction with reagents which must be used. In the discussions which follow it is understood that osmium and ruthenium are absent or have been removed in the manner indicated.

1. Separation by means of hydrogen sulfide

Palladium, rhodium, and platinum form insoluble sulfides in hot acid solutions of their chloro compounds, and thus, by precipitation with hydrogen sulfide, these metals can be separated from those elements which do not form insoluble sulfides. Iridium also forms a sulfide, but complete precipitation of it is difficult to attain. Precipitation with hydrogen sulfide does not separate the four named platinum metals from other elements which form insoluble sulfides in acid solution. The utilization of sulfide precipitation, therefore, is limited and applicable only to certain combinations of elements.

2. Separation by means of reduction to metal

Palladium, rhodium, and platinum are precipitated as finely divided metals by the reducing action of various reagents, such as formic acid, hydrazine, zinc, magnesium, etc. The complete reduction of compounds of iridium is difficult to accomplish. In certain instances separations based on reduction to metal can be effected. As a means of general separation, however, reduction to metal is not recommended.

3. Utilization of hydrolytic reactions in the separation of the platinum metals from other elements

The best general method for the separation of the platinum metals from the base metals with which they are usually associated is the hydrolytic precipitation of the base metals in a solution which is treated with sodium nitrite. If a solution which contains platinum, rhodium, and iridium, in the form of their chloro compounds, is treated with sodium nitrite and heated, the chloro compounds are converted to nitrito compounds. The complex compounds formed are $Na_2[Pt(NO_2)_6]$, $Na_3[Rh(NO_2)_6]$, and $Na_3[Ir(NO_2)_6]$. Each of these three compounds is quite stable and is not decomposed in boiling solutions the alkalinities of which are between pH 12 and pH 14. The palladium complex, $Na_2[Pd(NO_2)_4]$, is stable at pH 8, but it begins to decompose, probably because of hydrolysis, with the deposition of a brown precipitate, at an alkalinity approaching pH 10, and it is probably all decomposed at a slightly higher alkalinity.

Many of the non-platinic elements form insoluble hydroxides or hydrated oxides when the concentration of hydrogen ion in solution is adjusted to within the range pH 1 to 10, and particularly within the range pH 8 to 10. It is thus possible to remove collectively a considerable number of base metals.

(a) Hydrolytic behavior of individual elements in solutions containing sodium nitrite

The following elements are quantitatively precipitated as hydrated oxides in boiling solutions containing sodium nitrite, at the end point of thymol blue (approximately pH 10): copper, zinc, indium, titanium, zirconium, hafnium, thorium, chromium, manganese, iron, cobalt, and nickel.

Bismuth and cadmium appear to be completely precipitated at the end point of xylenol blue (approximately pH 8), if carbonate is present.

Gold is precipitated as metal by the reducing action of nitrite. Complete precipitation of it is attained when the acid solution is neutralized to pH 6.

Precipitation of aluminum hydroxide is complete at the end point of brom cresol purple (approximately pH 6.3). At increasing alkalinities aluminum hydroxide becomes more and more soluble.

Precipitation of gallium hydroxide is complete at the end point of brom phenol blue (pH 4) and at the end point of chlor phenol red (pH 6). It is entirely redissolved at the end point of xylenol blue.

Uranium, if taken as uranyl nitrate, appears to be completely precipitated at the end point of xylenol blue.

The elements which are not precipitated in nitrite solution within the range pH 1 to 10 are the following: silver, if taken as nitrate; mercury; univalent thallium, germanium; and phosphate, arsenate, vanadate, selenate, tellurate, molybdate, tungstate, and rhenate, as sodium salts.

The acidic radicals do form precipitates with a number of metallic cations, and such compounds as lead phosphate, lead arsenate, lead vanadate, etc., deposit in the nitrite solution.

There is no alkalinity at which the hydroxide of bivalent lead is completely insoluble. Precipitation of lead as carbonate is essentially complete at pH 8; that of lead as phosphate is quantitative in the range pH 4 to 10; and that also of lead as chromate, at pH 6.3.

The hydrated oxide of tin becomes colloidal at alkalinities greater than pH 7. It is completely precipitated in filterable form in the range pH 1 to 6. In the case of tin, precipitation is best accomplished at pH 1.5 from a solution to which nitrite has not yet been added.

A method for the analysis of dental gold alloys, based on the use of nitrite, was published by Gilchrist (760), and a similar one for the analysis of alloys used in jewelry was described by Holzer and Zaussinger (393).

(b) Hydrolytic behavior of individual elements in solutions containing sodium bromate

A number of the elements react in a different manner if the solution contains sodium bromate, instead of sodium nitrite. Sodium bromate is an oxidizing reagent, and by means of it separations can be effected within the groups of elements the separation of which is accomplished through the use of nitrite.

As has been previously discussed, the quantitative separation of palladium, rhodium, and iridium from platinum is effected in a boiling solution containing bromate, when the alkalinity is within the range pH 6.3 to 8.

Gold, which is completely precipitated in nitrite solution, remains soluble in one containing bromate.

Chromium, which is precipitated as tervalent hydroxide in nitrite solution, is oxidized to the chromate state in slightly acid solutions which contain sodium bromate. This difference in behavior in the two media enables the analyst to make good use of chromium, particularly in the separation of lead from the platinum metals.

When the alkalinity of a solution which contains lead and bromate exceeds pH 7, the lead is quantitatively precipitated as hydrated lead dioxide, a reaction which is of value to the analyst.

The non-platinic elements mentioned in connection with precipitation in nitrite solution, other than those few which have just been discussed, behave in bromate solution as they do in nitrite solution, with the exception of cobalt, nickel, etc., which form products of a higher state of oxidation.

(c) Possibilities for separations under conditions of controlled alkalinity

The control of the alkalinity of a solution enables one to effect separations not only of many of the base metals from the platinum metals but, in certain instances, of base metals from one another. The extent to which controlled hydrolytic reactions, and also precipitation of definite compounds, are of value does not appear to have been fully appreciated in general analytical chemical work. A number of the possibilities for separation are here indicated. Others can be inferred from the behavior of related elements.

(*1*) Palladium, rhodium, iridium, and platinum can be separated from those elements which form insoluble hydrated oxides in solutions containing sodium nitrite.

(*2*) Chromium can be separated from those elements which form insoluble hydrated oxides in solutions containing sodium bromate.

(*3*) Lead can be separated from palladium, rhodium, iridium, and platinum, by precipitation as lead chromate, in solutions containing sodium nitrite.

(*4*) Lead can be separated, by means of sodium bromate, from those elements which form oxy acids.

(*5*) Copper can be separated from arsenic, selenium, and tellurium in solutions containing either sodium nitrite or sodium bromate.

(*6*) Arsenic can be separated from palladium, rhodium, and iridium in solutions containing sodium bromate.

(*7*) Vanadium can be separated from aluminum, titanium, manganese, iron, cobalt, nickel, palladium, rhodium, and iridium in solutions containing sodium bromate.

(*8*) Mercury can be separated from copper and zinc in solutions containing sodium nitrite.

(*9*) Germanium can be separated from gallium and indium, and gallium can be separated from indium, merely by adjusting the alkalinity of the solution, without the aid of nitrite or bromate.

(*10*) Osmium and ruthenium can be separated, by hydrolytic precipitation of their hydrated oxides, from rhenium, which does not precipitate.

4. Utilization of fire-assay methods

The methods commonly used for the rapid evaluation of platiniferous materials have been those of fire assay. The value of fire-assay methods consists in the separation and collection of the platinum metals, the amount of which may be exceedingly small, from a large quantity of extraneous matter. In this respect these methods accomplish quickly what would otherwise be a tedious task. The difficulty with assay methods has been, however, that ultimately the separation of the platinum metals from one another must be effected by wet methods.

In 1936 Beamish and his associates in Canada attacked the problem of placing fire-assay methods for the platinum metals on a firm foundation. Their publications (636 to 644) constitute an outstanding contribution to this phase of analytical determination. In their work these investigators utilized hydrolytic methods of separation and thus combined the desirable features of fire-assay methods with those of the latest wet methods.

VII. ATOMIC WEIGHTS OF THE PLATINUM METALS

Determination of the chemical atomic weights (783) of the platinum metals has rested almost exclusively on the preparation and analysis of complex compounds, for the most part the potassium and ammonium salts of the chloro and bromo acids. In addition, the ammines have been utilized in the cases of rhodium, palladium, and ruthenium. In only one instance has a determination been made by ascertaining the metallic content of an oxide, namely, that of ruthenium dioxide, RuO_2.

In the years just preceding the outbreak of the World War of 1914, the chief center of activity on the atomic weights of the platinum metals was Gutbier's laboratory at the University of Erlangen.

A. DETERMINATION OF ATOMIC WEIGHTS BEFORE 1915

With the exception of two published accounts (337, 751), all of the work on the chemical atomic weights of the platinum metals was done prior to 1915. A brief review of it is here given.

1. Ruthenium

The atomic weight of ruthenium was determined first by Claus, the discoverer of ruthenium, who prepared K_2RuCl_5, the true composition of which was not clarified until about fifteen years ago. Later than Claus, Joly determined the ruthenium content of RuO_2, of $RuCl_3NO \cdot H_2O$, and of $(NH_4)_2[RuCl_5NO]$. In 1912 Vogt redetermined the ruthenium content of RuO_2.

2. *Rhodium*

The first determination of the atomic weight of rhodium was made by Berzelius, who prepared $Na_3[RhCl_6]$ and K_2RhCl_5. He calculated the atomic weight from the percentages of rhodium, chlorine, and of sodium chloride and potassium chloride, and likewise obtained ratios between the rhodium and chlorine, sodium chloride, and potassium chloride. Berzelius' methods became the standard pattern for all subsequent work of this type.

Jörgensen determined rhodium in chloropentamminerhodium chloride, $[Rh(NH_3)_5Cl]Cl_2$, and Seubert and Kobbe repeated the work, as did also Hüttlinger, and Dittmar. Renz determined rhodium in $[Rh(NH_3)_5Br]Br_2$.

3. *Palladium*

Berzelius' first attempt to obtain the atomic weight of palladium was with palladium sulfide. Later, he analyzed $K_2[PdCl_4]$ for Pd, 2KCl, and Cl_2. Keiser determined the palladium content of $[Pd(NH_3)_2Cl_2]$. This determination was subsequently repeated by Bailey and Lamb, and by Keller and Smith. Joly and Leidié, in their work, returned to the compound $K_2[PdCl_4]$.

Hardin obtained the metal content of $[Pd(C_6H_5NH_2)_2Cl_2]$, $[Pd(C_6H_5NH_2)_2Br_2]$, and $(NH_4)_2[PdBr_4]$.

Amberg utilized $[Pd(NH_3)_2Cl_2]$ and determined the ratio $2AgCl : [Pd(NH_3)_2Cl_2]$, as well as the palladium content. Krell, and also Woernle, determined the quantity of metal in $[Pd(NH_3)_2Cl_2]$, while Haas did the same with $[Pd(NH_3)_2Br_2]$, as also did Gebhardt. Kemmerer repeated the determination of palladium in $[Pd(NH_3)_2Cl_2]$ and, in addition, obtained that in $[Pd(NH_3)_2(CN)_2]$. The last work on $[Pd(NH_3)_2Cl_2]$ was done by Shinn.

4. *Osmium*

The atomic weight of osmium was determined by Berzelius, by Fremy, by Seubert, and by Seybold. Berzelius determined the amount of osmium and of potassium chloride in $K_2[OsCl_6]$. Fremy's results were based on the composition of OsO_4. The work upon which the atomic weight of osmium rested for many years was that of Seubert, who prepared and analyzed $K_2[OsCl_6]$ and $(NH_4)_2[OsCl_6]$. In 1912 Seybold reported the osmium content of $(NH_4)_2[OsCl_6]$.

5. *Iridium*

As usual, the earliest determination of the atomic weight of iridium was made by Berzelius, who analyzed $K_2[IrCl_6]$. This was followed by that of Seubert, who, in addition, analyzed $(NH_4)_2[IrCl_6]$. Joly determined the amount of iridium and of potassium chloride in $K_3[IrCl_6] \cdot 3H_2O$, and of iridium in $(NH_4)_3[IrCl_6]$. Hoyermann, and also Holzmann, repeated the work of Seubert on the determination of the iridium content of $(NH_4)_2[IrCl_6]$. Archibald, in 1909, published a preliminary note on the analysis of $K_2[IrCl_6]$.

6. *Platinum*

Berzelius determined the metal content of platinous chloride, and later studied $K_2[PtCl_6]$, which compound was also analyzed by Andrews. Seubert analyzed $(NH_4)_2[PtCl_6]$ and $K_2[PtCl_6]$. Halberstadt also utilized these compounds and, in addition, the corresponding bromo salts, as well as $PtBr_4$. This work was followed by that of Dittmar and McArthur on $K_2[PtCl_6]$.

The most thoroughly conducted and reliable work on the atomic weight of platinum was that of Archibald in 1909.

B. DETERMINATION OF ATOMIC WEIGHTS SINCE 1915

Very little interest has been taken in the determination of the atomic weights of the platinum metals by the usual chemical methods during the past quarter of a century. Only two pieces of work were published, that of Gilchrist (751) on osmium, and that of Gleu and Rehm (337) on ruthenium.

The chief interest during this period has been that of physicists, who, from a knowledge of the number, mass, and proportion (809) of the isotopes, have calculated values which, in the cases of platinum and rhodium, agree with those determined chemically. The recently determined chemical value of Gleu and Rehm for ruthenium is in agreement with that determined earlier by Aston.

Sampson and Bleakney (808) reported the value for palladium as 106.6; for iridium, as 192.2; for rhodium, as 102.89; and for platinum, as 195.23. The chemically determined values are 106.7, 193.1, 102.91, and 195.23, respectively.

Nier (804) redetermined the isotopic abundance ratios of osmium, using osmium tetroxide. These led to an atomic weight of 190.21 (packing fraction, -1×10^{-4}; conversion factor, 1.00027), which is considerably lower than that found by Gilchrist (751), 191.5, the accepted value from 1935 to 1938, from the osmium content of $(NH_4)_2[OsCl_6]$ and of $(NH_4)_2[OsBr_6]$.

Gleu and Rehm (337) reported the atomic weight of ruthenium as 101.1, from the ruthenium content of $[Ru(NH_3)_5Cl]Cl_2$.

In this connection, it is interesting to note that the atomic weight of gold, a metal closely related to platinum, as determined by physical means (781) has a value of 196.99. The long-accepted chemical value is 197.2.

The discrepancies which exist between the chemically determined atomic weights of osmium and of iridium and those calculated from estimates of isotopic ratios need to be cleared up. Unfortunately, there are few possibilities for obtaining the chemical atomic weights of the platinum metals by determining the metallic content of their oxides. In the case of osmium, its tetroxide might be considered, as Fremy tried to do years ago. Here, however, one is handicapped by the small ratio involved and by the difficulties which arise in handling such an unstable compound.

VIII. CONSTITUTION OF COMPOUNDS OF THE PLATINUM METALS

To gain any sort of an understanding of the chemistry of the platinum metals, it is necessary to think in terms of coördination compounds. There appears to be no other way by which to grasp easily a clear idea of the complicated reactions encountered. In that which is presented here, no attempt has been made to include intricate details of conditions under which various reactions and transformations are conducted. Such matters are fully described in publications by the original authors. Rather, the purpose has been to assemble certain ideas and features concerning the complex nature of the compounds of the platinum metals for the benefit of those not particularly conversant with the subject of coördination compounds.

A. THE THEORY OF WERNER

When used in a chemical sense, the term "coördination" is applied to a mode of atomic linking first recognized by Alfred Werner (778). His theory, which he first suggested in 1891 and developed more fully in 1893, originated in an attempt to explain the structure of a series of so-called molecular or complex compounds formed by the combination of apparently saturated molecules, and especially the compounds which many salts form with ammonia. The hypotheses proposed by him in explanation of the results of his researches are embodied in the coördination theory, which affords a simple and comprehensive explanation of the chemical constitution of the most diverse types of metallic salts. In the chemistry of the metallic elements, and especially so in the case of the platinum metals, few generalizations have proved so fruitful as those based on the study of molecular compounds, that is, of those compounds formed by the union in stoichiometric ratio of otherwise saturated molecules themselves capable of independent existence. The coördination theory of Werner has proved far-reaching in its scope, and has been fully substantiated by both chemical and physical evidence.

According to Werner, without invoking any special theory of valency, neutral molecules or negatively charged ions are grouped or coördinated around a central atom in the "first sphere of attraction", or coördination sphere. The number of groups which may be so arranged about the central atom is the coördination number, and is a characteristic property of that atom. In general, the coördination number can assume only those values (2, 3, 4, 6, 8) which allow of spatially symmetrical arrangements, the values 6 and 4 being the most usual. Werner assigned definite positions in space to the groups in a coördination complex. Where these were 4, an arrangement at the points of a tetrahedron had already been established for carbon by van't Hoff, but Werner showed that a different arrangement must occur in the 4-coördinate compounds of platinum. These compounds of platinum are never optically active. Compounds of the type PtA_2B_2 occur in two geometrically isomeric forms, which is possible if the four groups are in the same plane with the central atom, but not if they occupy the corners of a tetrahedron. To the groups in a 6-coördinate complex, Werner assigned the simplest distribution in three dimensions, at the points of an octahedron, and justified this by showing that certain compounds, which on this assumption must have asymmetric molecules, could be resolved into optically active forms.

The compound $[Pt(NH_3)_6]Cl_4$ is capable of ionizing into the complex ion

$[Pt(NH_3)_6]^{4+}$, with a net positive charge of four units, and four Cl^- ions. In such a compound Werner regarded the chlorine as bound in the "second sphere of attraction".

1. Ammines of the platinum metals

All the metals of the platinum group form ammines, that is, compounds in which ammonia is bound to the metallic atom. The following compounds of quadrivalent platinum and of bivalent platinum will serve as illustrations:

Derivatives of quadrivalent (6-coördinate) platinum

Hexammineplatinic chloride	$[Pt(NH_3)_6]Cl_4$
Chloropentammineplatinic chloride	$[Pt(NH_3)_5Cl]Cl_3$
Dichlorotetrammineplatinic chloride	$[Pt(NH_3)_4Cl_2]Cl_2$
Trichlorotriammineplatinic chloride	$[Pt(NH_3)_3Cl_3]Cl$
Tetrachlorodiammineplatinum (*cis*- and *trans*-isomers)	$[Pt(NH_3)_2Cl_4]$
Potassium pentachloroammineplatinate	$[Pt(NH_3)Cl_5]K$
Potassium hexachloroplatinate	$[PtCl_6]K_2$

Derivatives of bivalent (4-coördinate) platinum

Tetrammineplatinous chloride	$[Pt(NH_3)_4]Cl_2$
Chlorotriammineplatinous chloride	$[Pt(NH_3)_3Cl]Cl$
Dichlorodiammineplatinum (*cis*- and *trans*-isomers)	$[Pt(NH_3)_2Cl_2]$
Potassium trichloroammineplatinite	$[Pt(NH_3)Cl_3]K$
Potassium tetrachloroplatinite	$[PtCl_4]K_2$

The value of the molecular conductivity at 25°C. at infinite dilution is found to be 523 for hexammineplatinic chloride, which indicates dissociation of the compound into five ions. With succeeding substitution the conductivity falls to values consistent with four ions, three ions, two ions, and no ions. Zero conductivity corresponds to the compound $[Pt(NH_3)_2Cl_4]$, which consists only of the nullvalent coördinate complex. The further entrance of a chloride ion into the complex results in a net charge on it of one negative unit, and the dissociation of the compound into two ions. The end member of the series is the familiar $K_2[PtCl_6]$, which dissociates into three ions with a conductivity of 256. As will be seen later, the nullvalent compounds have a special interest.

2. Nomenclature of coördinate compounds

The nomenclature devised by Werner still regulates the naming of coördination compounds and its value lies in the fact that it permits uniform treatment of the whole range of compounds. An alteration is needed only as regards the indication of valency.

In the case of complex cations, the constituents of the complex are taken first, and the atoms or groups coördinated are mentioned in the order *(1) acidic groups*, such as chloro (Cl), cyano (CN), cyanato (NCO), thiocyanato (NCS), sulfato (SO_4), sulfito (SO_3), carbonato (CO_3), nitro (NO_2), nitrito (ONO), oxalato (C_2O_4), and hydroxo (OH); *(2) neutral groups*, such as aquo (H_2O), pyridino (C_5H_5N), and substituted amines ($C_2H_4(NH_2)_2$); and *(3)* last of all, preceding the metal itself, ammine (NH_3).

The names of the constituents of the complex are written as one word. It is to be noted that the ammonia molecule is designated as "ammine" and spelled with a double "m" to distinguish the word from "amine", which refers to a substituted ammonia. The Greek prefixes di, tri, tetra, penta, hexa, etc., are used to indicate the number of each coördinated group, the prefix mono being self-evident and unnecessary. For example, $[Pt(NH_3)_3py_2Cl]Cl_3$ would be named chlorodipyridinotriammineplatinic chloride. If the central atom is in the anionic complex, as it is in $K[Pt(NH_3)Cl_5]$ and $K_2[PtCl_6]$, the compounds are named potassium pentachloroammineplatinate and potassium hexachloroplatinate, respectively, the names of the constituents of the complex again being written as one word. In the case of nullvalent complexes, such as $[Pt(NH_3)_2Cl_4]$ and $[Pt(NH_3)_2Cl_2]$, the names are written tetrachlorodiammineplatinum and dichlorodiammineplatinum, again as one word.

While the above system of nomenclature serves admirably well, a more precise designation of the valency of the central atom is needed, and the Committee of the International Union of Chemistry for the Reform of Inorganic Chemical Nomenclature has so recommended (797). Instead of designating the valency of the central atom by -ous and -ic, the Committee has proposed the use of Roman figures expressing the valency to be placed in parentheses after the names of the elements to which they refer. $[Pt(NH_3)_5Cl]Cl_3$ would thus be named chloropentammineplatinum(IV) chloride, and $[Pt(NH_3)_3Cl]Cl$, chlorotriammineplatinum(II) chloride. In the case of complex anions of acids or salts, the valency of the central atom is given in parentheses after the name of the complex which ends in -ate. The Latin names of metals must often be used in this connection for reasons of euphony. $K_2[PtCl_6]$ would be called potassium hexachloroplatinate(IV), and $K_2[PtCl_4]$, potassium tetrachloroplatinate(II). By these rules, potassium ferrocyanide, $K_4[Fe(CN)_6]$, and potassium ferricyanide, $K_3[Fe(CN)_6]$, become potassium hexacyanoferrate(II) and potassium hexacyanoferrate(III), respectively. Potassium cobaltinitrite, $K_3[Co(NO_2)_6]$, becomes potassium hexanitritocobaltate(III). Mention of the valency of the central atom is not necessary when the number of ionized atoms or groups is given in the name as, for example, $[Pt(NH_3)_6]Cl_4$, hexammineplatinum tetrachloride; $K_4[Fe(CN)_6]$, tetrapotassium hexacyanoferrate; $K_3[Fe(CN)_6]$, tripotassium hexacyanoferrate. This last-named method of naming is to be recommended only in those cases where the electrochemical valency of the central atom is not known or is not known with certainty as, for instance, with compounds containing NO in the complex, such as $K_2[RuCl_5NO]$. In the case of the nullvalent complexes $[Pt(NH_3)_2Cl_4]$ and $[Pt(NH_3)_2Cl_2]$, it is not necessary to give the valency of the central atom.

3. Groups which behave like ammonia in the coördination sphere

Although ammonia was the first of the neutral nitrogen compounds to be introduced into the coördination complex, it is not the only one in which the coördinating ability of nitrogen has been utilized. Certain other compounds of nitrogen have even more interest for the chemist than has ammonia. Besides nitrogen compounds, those containing sulfur, selenium, phosphorus, and arsenic have been used as neutral coördinating groups. The following list will give the reader an idea of the types of compounds which have been used in preparing coördination compounds of the platinum metals.

(a) Organic compounds containing nitrogen

Amines: Methyl-, ethyl-, propyl-, butyl-, and amyl-amines; benzylamine, phenylamine (aniline), toluidine, xylidine, *p*-phenetidine; diethyl- and dipropylallylamines; 1,2,3-triaminopropane; ethylenediamine, propylenediamine.

Amidines: Guanidine.

Amino acids: Glycine.

Nitriles: Propionitrile, benzonitrile; 1,2-dicyanobenzene, 1,2-dicyanonaphthalene.

Isonitriles: Methyl-, butyl-, and phenyl-carbylamines.

Dioximes: Dimethylglyoxime.

Compounds containing nitrogen in the ring: Pyridine, picoline, lutidine, collidine, piperidine; quinoline; pyrazole, glyoxaline; 2,2′-dipyridyl; 2,2′2″-tripyridyl, *o*-phenanthroline; pilocarpine, nicotine, strychnine, brucine.

(b) Organic compounds containing sulfur

Methyl, ethyl, propyl, butyl, and benzyl sulfides; diethylene disulfide; dimethyl-, diethyl-, dipropyl-, and dibutyl-dithioethyleneglycols; diethyl- and dipropyl-dithiotrimethyleneglycols; thiocarbamide (thiourea), methyl-, ethyl-, and undecyl-thiocarbamides; diethyl- and triethyl-thiocarbamides; thioacetamide; xanthogenamide.

(c) Organic compounds containing selenium, tellurium, arsenic, and phosphorus

Ethyl selenide; diethyldiselenotrimethyleneglycol; triethylarsine; trimethylphosphine and triethylphosphine.

4. Abbreviations commonly used

To save time and confusion in writing formulas, it has been necessary to make use of abbreviations, or more properly symbols, to indicate many of the coordinating groups. The more familiar ones encountered in the literature are listed below:

SYMBOL	COÖRDINATING GROUP	SYMBOL	COÖRDINATING GROUP
ac	Acetylacetone	py	Pyridine
ec	Ethylenediaminebisacetylacetone	qu	Quinoline
en	Ethylenediamine	pic	Picoline
et	Ethylene	tu	Thiourea
etn	Ethylamine	tpn	1,2,3-Triaminopropane
etu	Ethylenethiourea	tren	Tri-(β-aminoethyl)amine
hx	Hydroxylamine	phenan	o-Phenanthroline
ox	Oxalate radical	dipy	Dipyridyl
mn	Methylamine	tripy	Tripyridyl

B. MANIFOLD ASSOCIATING GROUPS

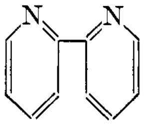
Among the various associating groups which have been mentioned there are some which differ from ammonia in having the ability to fill more than one position in the coördination complex, and it is this property that makes them of interest and use in the study of structure.

1. Unidentate (unifunctional) groups

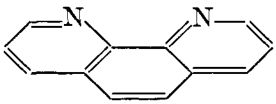
In $[Pt(NH_3)_6]Cl_4$ the ammonia molecule and in $[PtCl_6]K_2$ the chloride ion each occupy only one position within the coördination sphere, and a similar degree of association is manifested by water, the hydroxo group, oxygen, pyridine, methylamine, dialkyl or diaryl sulfide, phosphine, arsine, and many other molecular species.

2. Bidentate (bifunctional) groups

Compounds such as ethylenediamine, $NH_2CH_2CH_2NH_2$, and radicals such as the oxalato group, C_2O_4, each of which functions in the coördination sphere as two associating units or doubly bound groups, often to form exceedingly stable coördination compounds, have been classed by Sir Gilbert Morgan (802) under the convenient general term of chelate groups, after the Greek noun, singular, ἡ χηλή, a cloven hoof, as of an ox; plural, αἱ χηλαί, as of a crab's claws. Certain of these chelate groups have played an important part in the demonstration of the stereochemical structure of coördination compounds. 2,2′-Dipyridyl,



and o-phenanthroline,



furnish examples of such chelate groups, both of which were employed by Werner in the demonstration of octahedral structure. The orange-red bivalent ruthenium salt $[Rudipy_3]Cl_2 \cdot 6H_2O$ was found by Burstall (542) to be sufficiently stable for resolution into optically active forms.

Chelate groups need not be organic, as was demonstrated by Werner in the case of hexoldodecamminetetracobaltic chloride, and by Mann in the case of the sulfamide compound of rhodium, both of which are discussed later under the heading of inorganic optical activity.

3. Tridentate and quadridentate groups

In addition to the numerous bifunctional chelating groups there are a few compounds known which are capable of filling three (tridentate or trifunctional groups) or even four (quadridentate or quadrifunctional groups) positions in the coördination sphere.

As typical tridentate groups there may be cited tripyridyl and 1,2,3-triaminopropane. These form very stable compounds with the 6-coördinate metals, of the types $[Mtripy_2]X_n$ and $[Rhtpn_2]I_3$ (543). In such compounds the coördinated group is probably attached in the 1,2,6-positions along the octahedron edge, as shown by the fact that the same tridentate groups readily fill three coördination positions in the planar 4-coördinate complex, as in [Pt tripyCl]Cl. It can be shown that such a structure is strainless only if the platinum atom and the whole tripyridyl molecule are coplanar.

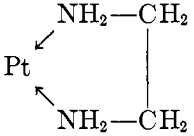
A fourfold associating unit is furnished by the bivalent radical of ethylenediaminebis(acetylacetone), $\{CH_2N:C(CH_3)CH:C(OH)CH_3\}_2$, which forms a remarkably stable complex with palladium. Tri(β-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$, also behaves as a fourfold associating compound and gives rise to the platinum salts $[Pttren]I_2$ and $[PtCl_2tren]Cl_2$.

The subject of quadridentate groups should not be dismissed without mention of the particularly important metallic derivatives of the porphyrin skeleton. These compounds are deeply involved in the vital processes of both the vegetable and the animal kingdoms. Chlorophyll, and the hemin of blood, contain the magnesium and iron inner complex salts of porphyrin derivatives. A similar type of derivatives is known as the phthalocyanines, a series of metallic complexes of great stability conveniently produced by heating a metal or its chloride with 1,2-dicyanobenzene. In the phthalocyanine, as in the porphyrin, the coördinating group forms a rigid planar structure of just such dimensions as to accommodate a metal ion.

4. Ring size and chelation

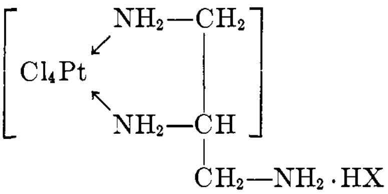
For a molecule with two potentially coördinating groups, such as a diamine, $NH_2(CH_2)_nNH_2$, or an amino acid, $NH_2(CH_2)_nCOOH$, to function as a chelate group, it must be geometrically possible to form a ring of low strain, precisely as in the formation of carbon rings in organic chemistry. Chelation will therefore be most favored when the groups are in the 1,4- or the 1,5-positions.

Where saturated (single-linked) rings are formed, as by the coördination of diamines, the five-membered ring,

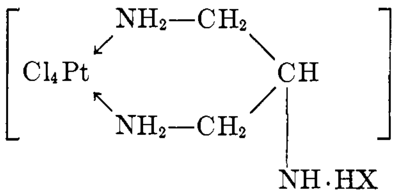


as formed by ethylenediamine, is the most stable. Objective proof of this was furnished by Drew (574), who found that ethylenediamine and, less readily, 1,3-propylenediamine coördinate with platinum, whereas the higher polymethylenediamines form only amorphous ill-defined products, in which the two amino groups of any one molecule of diamine are probably linked to different metallic atoms.

A demonstration of the superior stability of the five-membered, as compared with the six-membered, ring was given by Mann (546) in studying the coördination compounds of 1,2,3-triaminopropane, $NH_2CH_2CH(NH_2)CH_2NH_2$. This compound *can* react so as to occupy *only two* coördination positions, the third amino group then being capable of salt formation. The compound of this type formed with platinic chloride will then be asymmetric,



or symmetrical,



according as a five-membered ring or a six-membered ring is formed preferentially by chelation. Mann resolved the compound into optical isomers, thereby establishing the structure with a five-membered chelate ring.

Where chelate rings involving double bonds are formed, the formation of six-membered rings is favored. It is thus the β-diketones which most readily give rise to inner complex salts.

Determinations of the configuration of stereoisomeric series depend on the fact that bifunctional groups, such as ethylenediamine or the oxalato group, can, from considerations of molecular dimensions, span only *cis*, or 1,2-, positions. Hence, provided that no intramolecular change of configuration occurs during reaction, the isomer which is capable of reacting with a chelating group must belong to the *cis*-series.

C. ISOMERISM

In considering coördination compounds, it soon becomes apparent that a number of types of isomerism are possible.

1. Ionization isomerism

Examples of a type of isomerism which Werner termed ionization isomerism are the violet red $[Co(NH_3)_5Br]SO_4$ and the red $[Co(NH_3)_5SO_4]Br$; $[Co(NH_3)_5Br]C_2O_4$ and $[Co(NH_3)_5C_2O_4]Br$; $[Pt(NH_3)_4(OH)Cl]SO_4$ and $[Pt(NH_3)_4(OH)SO_4]Cl$; $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$.

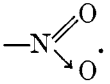
It is important to note that in certain cases dibasic acid radicals may occupy only one position in the coördination complex. While occupying only one coördination position and being un-ionized, the sulfato group neutralizes two of the ionic charges on the cobalt, making the whole complex ion univalent. In the example cited, the oxalato group behaves in a similar manner.

2. Salt isomerism

A type of isomerism associated with the potential existence of isomeric forms of the acid radical bound within the complex was termed salt isomerism by Werner. This is exemplified by the unstable scarlet $[Co(NH_3)_5(ONO)](NO_3)_3$ and the stable yellow-brown $[Co(NH_3)_5NO_2](NO_3)_3$. Other examples are the unstable *cis- and trans-* $[Coen_2(ONO)_2]X$ and the corresponding nitro compounds, $[Coen_2(NO_2)_2]X$; the unstable $[Copy_2(NH_3)_2(ONO)_2]X$ and the stable $[Copy_2(NH_3)_2(NO_2)_2]X$.

Although no examples were noted in the literature, this type of isomerism presumably exists in the case of the platinum metals.

The only apparent seat of isomerism is in the $—NO_2$ group, which might, as in the organic nitrous esters and nitro compounds, react either as $—O—N{=}O$ or as



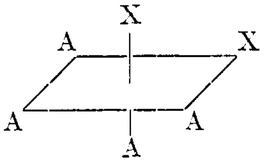
$—N\begin{smallmatrix} /\!\!/ O \\ \searrow O \end{smallmatrix}$.

3. Stereoisomerism

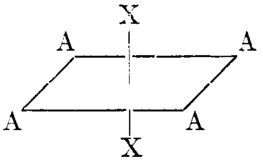
In harmony with Werner's conception of the equivalence of the coördination positions, it has been seen that complex ions of the type $[MA_5B]$, where A is NH_3 and B is H_2O or Cl, exist in only one form except where salt isomerism occurs. The substitution of a second group, giving a complex of the type $[MA_4XY]$, must lead to the possibility of stereoisomerism and the number of isomers should indicate the spatial arrangement of the groups. A regular octahedral arrangement leads to two disubstituted products, 1,2 and 1,6.

(a) *Cis–trans* isomerism

In the 6-coördinate complexes of quadrivalent platinum, and in the 4-coordinate complexes of bivalent platinum, as examples, the possibility of *cis–trans* isomerism exists. In the octahedral arrangement of the 6-coördinate complex, the two spatial groupings of the disubstituted product may be represented as follows:



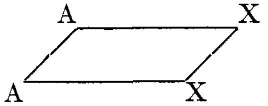
Cis-form



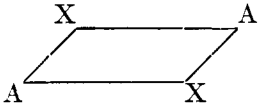
Trans-form

Thus, in the diacidotetrammine complex of quadrivalent platinum, $[Pt(NH_3)_4Cl_2]^{2+}$, and in the tetraacidodiammine complex, $[Pt(NH_3)_2Cl_4]$, *cis–trans* isomerism may be expected.

In the 4-coördinate complex, on the planar basis, the groupings are as follows:



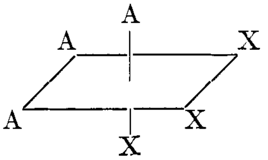
Cis-form

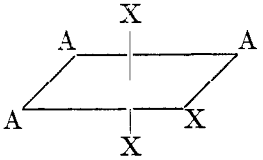


Trans-form

Examples of these arrangements are the *cis–trans* forms of dichlorodiammineplatinum, $[Pt(NH_3)_2Cl_2]$, and of dichlorodiamminepalladium, $[Pd(NH_3)_2Cl_2]$.

In the 6-coördinate triacidotriammine complexes the existence of two geometrically isomeric forms should be possible, for instance:

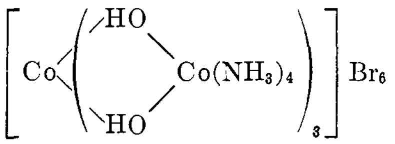




In the case of tervalent metals the complex is nullvalent.

(b) Optical isomerism

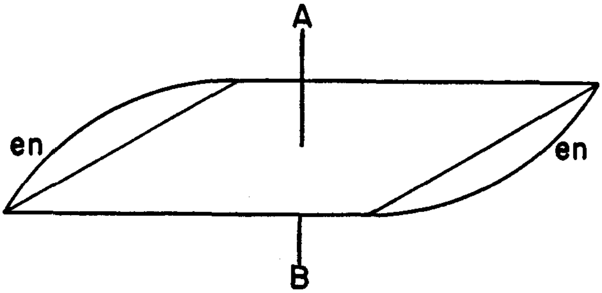
The crowning achievement of Werner's theory of coördination was the prediction of optically active compounds. In 1911 Werner accomplished the resolution of cobalt compounds with two and three chelate groups, such as $[Coen_2(NH_3)Cl]X_2$, $[Coen_2(NO_2)Cl]X$, and $[Coen_3]X_3$, into their optical antimers, and thus established his octahedral theory for cobalt. To prove that the optical activity was not caused by some rearrangement of the organic groups involved, he succeeded in 1914 in resolving the purely inorganic compound



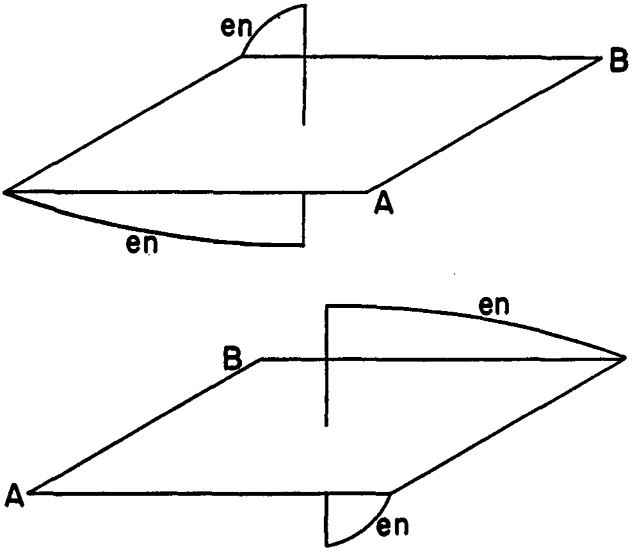
$$\left[\mathrm{Co}\left(\begin{array}{c}\mathrm{HO}\\ \\ \mathrm{HO}\end{array}\mathrm{Co(NH_3)_4}\right)_3\right]\mathrm{Br}_6$$

He further prepared optically active compounds containing chromium, iron, and rhodium. In 1917 Delépine (479) effected the resolution of $K_3[Ir(C_2O_4)_3]$.

The octahedral configuration of the 6-coördinate complex requires the existence not only of geometrical isomerism of the kinds previously mentioned, but also of mirror-like isomerism, leading to optical activity.



Trans-form

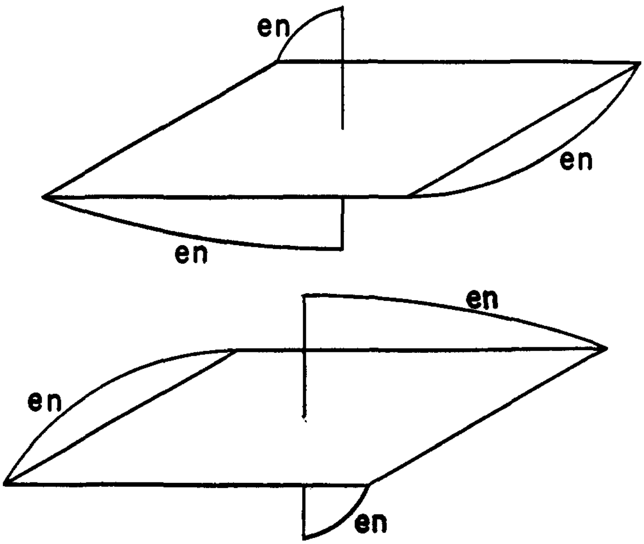


Cis-forms

The *trans*-form of the complex [Rhen$_2$AB] possesses a plane of symmetry, and so must be non-resolvable. The one *cis*-form is not superposable upon its mirror image, and the two optical isomers should be capable of resolution.

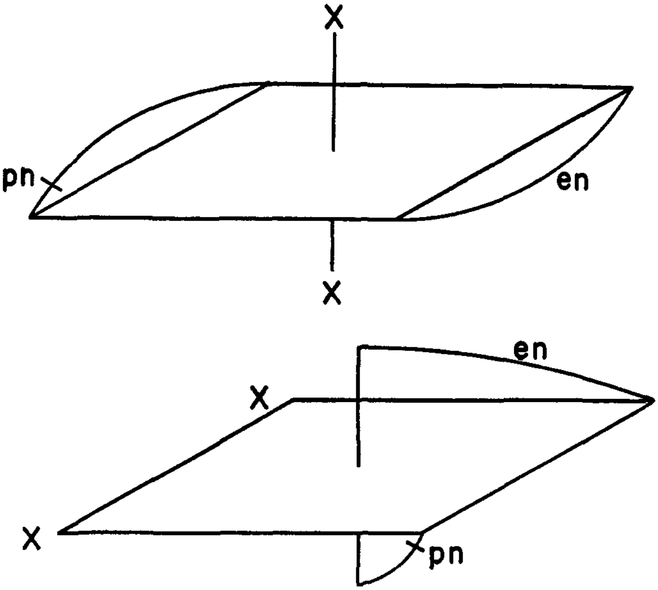
The molecular dissymmetry does not vanish if A = B. For the maintenance of dissymmetry it is not even necessary that two chelating groups should be present. *Cis*-compounds of the type [M^{III}enA$_2$B$_2$] must also display optical activity.

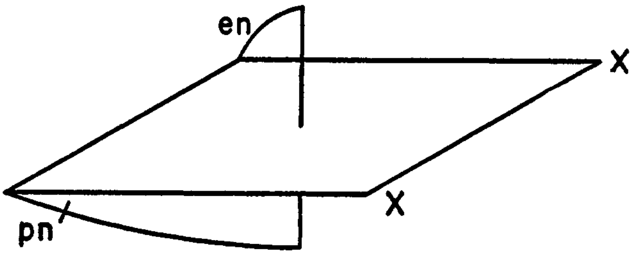
When three bifunctional chelating groups are introduced into the 6-coördinate complex, there is no asymmetry of any one atom but there exist only "odd" symmetry elements of the whole molecule, in the form of trigonal axes of symmetry through the centers of the octahedron faces.

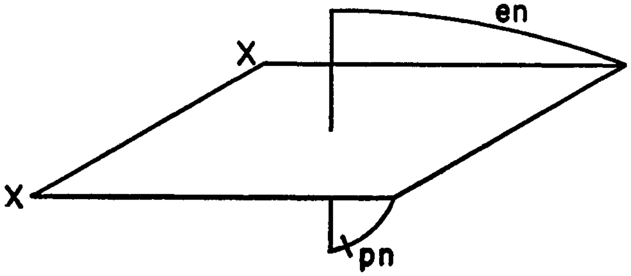


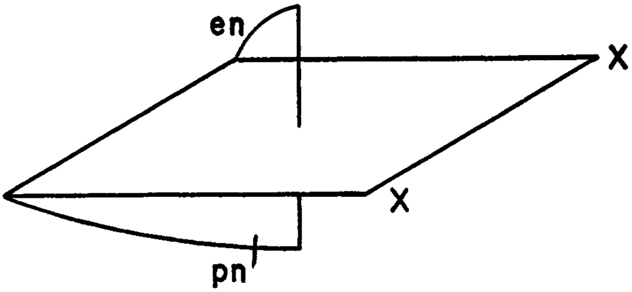
The trioxalato complexes, in which the oxalate radical acts as a chelating group, are similar in symmetry to those of the trisethylenediamino complexes.

Where an *existing* asymmetric center is introduced into a complex, the possibilities of isomerism are greatly increased, and cases arise which have no counterpart in the stereochemistry of carbon. Propylenediamine, $NH_2CH_2CH(CH_3)NH_2$, which contains an asymmetric carbon atom, may enter into combination either in its dextro- or its levo-form. The *trans*-complex, itself not asymmetric, may then be formed either with *d*- or with *l*-pn, while two distinct series of the *cis*-isomers should exist.

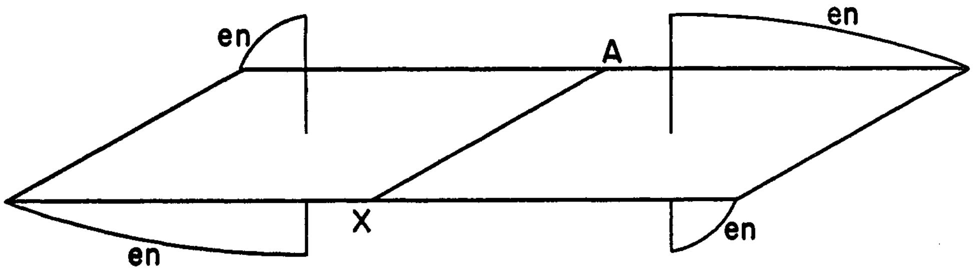




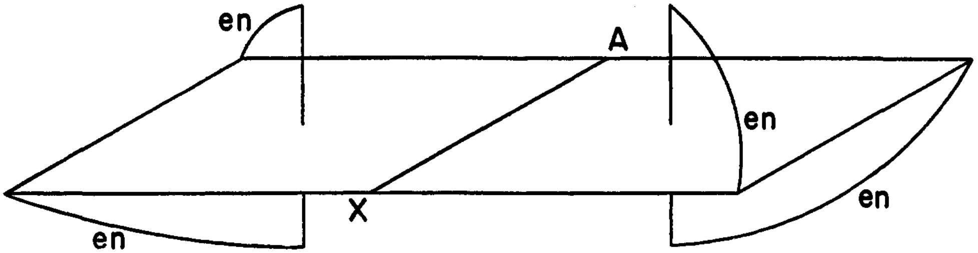




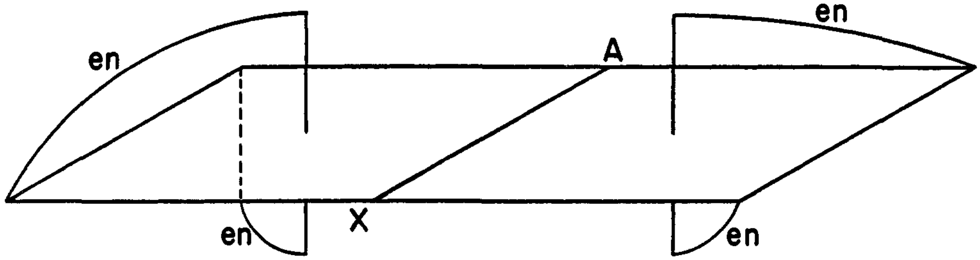
In binuclear complexes it is possible to have two asymmetric centers in the molecule. If the asymmetric centers are structurally similar, there should exist an internally compensated or meso form, in addition to the dextro- and levo-rotatory isomers. The case is analogous to that of tartaric acid among the active carbon compounds.



Inactive meso form



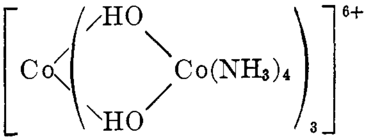
Dextro form



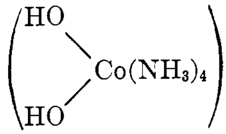
Levo form

(c) Purely inorganic compounds which exhibit optical activity

In those cases of optical activity which have just been mentioned, the complexes have contained coördinated carbon compounds in the form of chelating groups such as the oxalate radical, ethylenediamine, dipyridyl, etc. It is only natural that the question should arise as to whether optical activity would be displayed by the introduction of chelating groups which are purely inorganic. So far, only two instances have been recorded of the successful resolution of purely inorganic compounds, namely that of Werner (811), in 1914, who resolved the hexoldodecamminecobaltic ion



by means of bromocamphorsulfonic acid, and that of Mann (556), in 1933, who resolved the sulfamide compound of rhodium by means of α-phenylethylamine.

In principle the polynuclear compound of Werner is analogous to the trisethylenediaminecobaltic salts, $[Coen_3]X_3$, the difference being that the group  , instead of ethylenediamine, functions as the chelating group.

Mann's compound is of the general type $[Men_2AB]$, with only two chelating groups. According to Mann, sulfamide, $SO_2(NH_2)_2$, in coördinating with rhodium and with platinum, functions as a dibasic acid, $[SO_2(NH)_2]H_2$, to form the compounds $[Rh(SO_2N_2H_2)_2(H_2O)]Na$ and $[Pt(SO_2N_2H_2)_2(OH)(NH_3)]Na$.

4. Coördination isomerism

Under the term "coördination isomerism" Werner lists compounds in which two central atoms, one in the positive complex and one in the negative complex, give rise to isomerism. Examples in which the two central atoms are different are the following: the violet $[Cu(NH_3)_4]^{II}[PtCl_4]^{II}$ and the green $[Pt(NH_3)_4]^{II}[CuCl_4]^{II}$; $[Zn(NH_3)_4]^{II}[PtCl_4]^{II}$ and $[Pt(NH_3)_4]^{II}[ZnCl_4]^{II}$; $[Cren_3]^{III}[Co(C_2O_4)_3]^{III}$ and $[Coen_3]^{III}[Cr(C_2O_4)_3]^{III}$. Examples in which the central atoms are the same but different in valency are: $[Pt(NH_3)_4]^{II}[PtCl_6]^{II}$ and $[Pt(NH_3)_4Cl_2]^{II}[PtCl_4]^{II}$; $[Ptpy_4]^{II}[PtCl_6]^{II}$ and $[Ptpy_2Cl_2]^{II}[PtCl_4]^{II}$. The isomeric pairs have the same empirical composition. The Roman numerals are here used to indicate the net charges of the complex ions.

In connection with compounds of this type, the number of known isomeric forms of certain of the planar compounds exceeds that permitted on the basis of the planar hypothesis. The cause of such anomalies has not yet been fully interpreted. The best known instance is that of the green salt of Magnus, $[Pt(NH_3)_4][PtCl_4]$, which also exists in an unstable red form. While it has been suggested that the red salt is not Magnus' salt, but is chlorotriammineplatinous chloroplatinite, $[Pt(NH_3)_3Cl]_2[PtCl_4]$, which, like $[Pt(NH_3)_4][PtCl_3(NH_3)]_2$ and $[Pt(NH_3)_3Cl][PtCl_3(NH_3)]$, has the same empirical formula, this view is not reconcilable with the work of Drew and Tress (582). As a matter of fact, either the green or the red form of $[Pt(NH_3)_4][PtCl_4]$ gives rise to grayish pink needles of $[Pt(NH_3)_4][PdCl_4]$, which are different from the golden brown plates of $[Pt(NH_3)_3Cl]_2[PdCl_4]$ produced from the red $[Pt(NH_3)_3Cl]_2[PtCl_4]$. The formation of the red salt of Magnus is favored, in general, in ammoniacal solutions, in which the triammine compound would be readily converted into the tetrammine compound. Although the individuality of the two forms is assured, the relation between them is not clear.

Other examples of anomalous isomerism exist in the case of the yellow and red forms of $[PtCl_2dipy]$ and in that of the yellow and red forms of $[Pd(NH_3)_2Cl_2]$ and $[Pd(NH_3)_2I_2]$.

5. The "isomeric chlorides" of ruthenium

Another instance of unexplained isomerism, with which Werner brought his book (778) to a close, was that supposed to exist among the chloro compounds of ruthenium.

Claus, the discoverer of ruthenium, prepared (785) two chloro salts of ruthenium to which he assigned the formulas K_2RuCl_5 and K_2RuCl_6. The first was formed when the precipitated oxide of ruthenium, or the volatile tetroxide, was dissolved in hydrochloric acid and treated with potassium chloride; the second, when aqua regia was used. Later (792, 796), it was shown that the supposed K_2RuCl_6 was a nitroso salt, K_2RuCl_5NO. The first salt has, since the time of Claus, passed for K_2RuCl_5, which was considered a pentachlororuthenite. Efforts to oxidize this salt to K_2RuCl_6 have been of no avail. Miolati and Tagiuri (801) reported a monohydrate of K_2RuCl_5.

In 1904 Howe (793) described a new monohydrate of K_2RuCl_5, which differed very markedly from the former salt in properties, especially in stability toward hydrolysis and in being converted into K_2RuCl_6 by the action of chlorine. It was formed from the earlier K_2RuCl_6 by boiling with dilute alcohol in acid solution, and was called an "aquo" salt. The corresponding rubidium and cesium salts were also prepared, as well as similar salts with bromine (794) in the place of chlorine. It was thus thought that there might be an instance of isomerism between these two series of pentachlororuthenites.

The explanation of this anomaly depended upon ascertaining the state of valency of the ruthenium in the two types of compounds, and in determining the composition of the salts, particularly with respect to water. Considerable confusion appeared to exist in ascertaining the state of valency. In reducing ruthenium solutions with zinc, hydrogen sulfide, and other agents, a conspicuous blue color is formed. Claus had regarded the color as that of bivalent ruthenium. Remy and Wagner (319) considered it to be that of univalent ruthenium and based their opinion on its being formed when the valency of the ruthenium in K_2RuCl_5 was reduced two units, as measured by the action of sodium amalgam. Zintl and Zaimis (813) also assumed the presence of univalent ruthenium in the blue solution, basing their view on the potentiometric titration of "$RuCl_3$" with chromous or titanous sulfate, where with one equivalent they obtained a pale yellow solution, while with the next drop the blue began to appear.

Charonnat (505) in 1925 suggested that the true formula for the ordinary pentachlororuthenite is $[K_2RuCl_5OH]$, basing his view on the action of this salt on potassium iodide, and on the formation of the aquo salt by the action of hydrochloric acid on the oxalato compound, $K_3[Ru(C_2O_4)_3]$. Charonnat, however, did not support his idea with details or analyses.

Howe's last paper (693) on the subject concludes that no isomerism exists and that the explanation lies in the fact that Claus' K_2RuCl_5 is in reality $K_2[RuCl_5OH]$, in which ruthenium is quadrivalent and that the aquo salt $K_2RuCl_5 \cdot H_2O$ is $K_2[RuCl_5H_2O]$, in which ruthenium is tervalent.

D. INNER COMPLEX SALTS

Of the different types of coördination compounds perhaps none interest the analytical chemist more than those which Werner termed inner complex salts.

It will be recalled that the non-electrolyte complexes, such as triacidotriamminecobalt and diacidodiamminepalladium, are formed by the attachment of an equal number of neutral groups and acidic radicals to the central atom. If the neutral group and the acid radical are united in the same molecule as, for example, in the case of glycine, NH_2CH_2COOH, the compounds formed have, in many cases, great stability, very low solubility in water, but high solubility in organic solvents. Non-electrolyte complexes of this kind are included in the term "inner complex salts" and are usually referred to as inner complex salts of the first order. They possess a considerable practical importance in that the formation of such compounds underlies the action of many of the so-called specific analytical reagents.

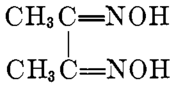
Cobaltic oxide reacts with solutions of glycine, forming a mixture of two compounds which are isomeric and have the composition $Co(NH_2CH_2COO)_3$. These compounds are remarkably stable. They may be dissolved without change in concentrated sulfuric acid; their solutions have practically no electrical conductivity; and cryoscopic measurements show that they are undissociated in solution. They represent the two geometrical isomers of trisglycinecobalt.

Glycine also forms inner complex salts with other metals, for example, with 4-coördinate copper. Pinkard, Sharratt, Wardlaw, and Cox (594) obtained *cis*- and *trans*-forms of diglycinepalladium.

A second, particularly important class of inner complex salts is that formed by the enolic form of β-diketones, for example, acetylacetone. The enol group is salt-forming, and the ketonic group then coördinates with the metal. The acetylacetonates are typical non-electrolytes. They are practically insoluble in water, but readily soluble in benzene.

The possibility of forming inner complex salts arises whenever donor (amino, thiol, or carbonyl groups) and acidic functions are suitably placed in the same molecule, that is, in 1,4- or 1,5-positions to one another. It is a remarkable and quite unexplained phenomenon that the presence of certain atomic groupings may confer the property of forming inner complex salts more or less specifically with some particular metal, that is, the inner complex salt formed by that metal is characterized above all others by its stability and, as a usual corollary, its insolubility in water.

Of particular interest to the platinum chemist is the atomic grouping of dimethylglyoxime,



$$\begin{array}{l} CH_3C{=}NOH \\ \quad\;\; | \\ CH_3C{=}NOH \end{array}$$

which forms inner complex salts with the 4-coördinate metals, bivalent palladium, bivalent platinum, and bivalent nickel. The discovery of these glyoxime compounds resulted, as was previously mentioned, from the first research made by Chugaev (1) on the platinum metals.

Mann (556) has indicated that chelating groups fall into two classes: (*1*) Those that can fill all six coördination positions, as can ethylenediamine or the oxalato group; (*2*) those which, while capable of filling four positions in the 4-coördinate complex, cannot fill more than four coördination positions when introduced into the 6-coördinate complex. Mann's sulfamide belongs to the second class of chelating compounds, and so does dimethylglyoxime. Chugaev showed that although dimethylglyoxime fills completely the four coördination positions about bivalent nickel, palladium, or platinum, compounds of the types $[Codmg_2(NH_3)_2]Cl$, $[Codmg_2(NO_2)_2]NH_4$, and $[Rhdmg_2(NH_3)_2]Cl$ are formed with the 6-coördinate metals cobalt and rhodium, in which it occupies four coördination positions. Herein, undoubtedly, lies the explanation of the clean-cut analytical separation of bivalent palladium from tervalent rhodium and tervalent iridium by dimethylglyoxime.

If the number of acido groups in the inner complex salt is not equal to the valency of the central atom, the resulting complex will itself be an ion. Werner termed compounds of this type inner complex salts of the second order. For instance, silicon, which is quadrivalent, has a coördination number of six. It forms a complex with three molecules of acetylacetone, $[Siac_3]Cl$, in which one valency of the silicon is unsaturated. The coördination complex thus forms a positive ion. With bivalent cobalt, the coördination number of which is six, the compound is $[Coac_3]Na$, and the complex is negative. In the case of bivalent platinum (coördination number four), the complex portion of the compound $[PtCl_2ac]K$ likewise is negative.

The tendency to form inner complex compounds of the second order is shown by organic hydroxy acids, such as tartaric and citric acids, with the result that they are often utilized to mask the usual reactions of the heavy metals.

E. ELECTRONIC INTERPRETATION OF COÖRDINATION

With the enunciation of the theory of the atomic number in 1913, wider interest in coördination compounds was awakened. The coördinate link of Werner took on a new significance and became firmly established as one of the three types of valency now recognized by chemists.

To obtain a clearer picture of coördination than has heretofore been presented in this discussion, it is necessary to review briefly the structure of the atom.

1. Arrangement of the electrons in the atom

The theory of atomic structure which is now almost universally accepted is that due to Rutherford, according to which the atom is built up of a small positively charged nucleus, surrounded by a sufficient number of electrons to render the whole structure electrically neutral. The positive charge of the nucleus of the uranium atom, the heaviest of atoms, is 92 times that of the hydrogen atom, the lightest of atoms. The atomic number of uranium is 92, that of hydrogen, 1.

Two views of the general nature of the electron are held. The first is that the electron in an atom is a minute particle with a mass 1/1840 the mass of the proton, and with a charge equal to $-e$, and moving in an orbit around the nucleus. The second and more recent view is that the electronic charge is not localized in a small element of space, but that there is a probability function which represents its distribution at any given instant. However, the idea of electrons moving in orbits of different energies is a satisfactory approximation for many physical and most chemical purposes.

The proper interpretation of the results of the analysis of the x-ray, ultraviolet, and visible spectra of the elements has given a complete picture of where every electron is situated and what the energy of its orbit is. Four quantum numbers which are necessary in assigning the electrons to their proper positions are: The principal quantum number n; the azimuthal quantum number l; the magnetic quantum number m; and the spin quantum number s. The first division of the electrons is made according to the principal quantum number n, which can have the values 1,2,3,4, etc. The corresponding shells are often designated K, L, M, N, etc. The azimuthal quantum number can have the values 0, 1, 2, 3, etc. Thus, there is a subdivision of energy levels within the shells K, L, M, N, etc. Electrons with $l = 0, 1, 2, 3$, are called s, p, d, f electrons, respectively. This nomenclature is a survival of an old and empirical notation (s for sharp, p for principal, d for diffuse, f for fundamental) which was based on the appearance of spectral lines caused by electron transitions involving these shells. The two other quantum numbers, m and s, are needed to account satisfactorily for all the observed lines in the spectra of an element.

In addition, a restriction known as the Pauli exclusion principle is likewise needed. According to this principle no two electrons in the same atom can have the same values for the four quantum numbers. This means that every electron in the atom differs from every other electron in total energy, and that there can be as many electrons in each of the shells as there are possible different arrangements of the quantum numbers. It is therefore found that the maximum numbers of electrons in the K, L, M, N, and O shells are 2, 8, 18, 32, and 50, respectively.

It is seen that the K shell, which can contain only two electrons, is completed in helium, and that all elements with more than two electrons have the K shell full. There are only eight possible orbits in the L shell, which is completed in neon, atomic number 10. Like neon, argon, krypton, xenon, and radon have their s and p orbits in their outermost shells completely filled. This configuration, usually called a closed shell, is very stable, and is of interest in the discussion of coördination compounds.

2. Electronic arrangement in the atoms of the metals of the eighth group of the Periodic System

In discussing the coördination compounds of the platinum metals, consideration should also be given to the members of the first triad of the eighth group of the Periodic System. The electronic arrangements of these nine metals, as well as those of krypton, xenon, and radon, may be written in the following abbreviated form, the completed electronic orbits being omitted. The corresponding atomic numbers are given in parentheses.

Fe (26) $3d^6 4s^2$	Co (27) $3d^7 4s^2$	Ni (28) $3d^8 4s^2$	Kr (36) $4s^2 4p^6$
Ru (44) $4d^7 5s^1$	Rh (45) $4d^8 5s^1$	Pd (46) $4d^{10}$	Xe (54) $5s^2 5p^6$
Os (76) $5d^6 6s^2$	Ir (77) $5d^7 6s^2$	Pt (78) $5d^9 6s^1$	Rn (86) $6s^2 6p^6$

It is to be noted that the outermost electronic distributions in iron and osmium are similar, as are also those in cobalt and iridium. Attention is likewise called to the electronic groupings in palladium and platinum, two elements which are usually regarded as very similar, but which differ markedly in their stable states of electrovalency.

3. The three types of valency recognized by chemists

The electronic conception of matter gives precision to the coördination theory, since it offers a simple explanation of the three manifestations of valency now recognized by chemists.

The essential feature of the electronic theory of valency is the conception of three types of binding between atoms: namely, electrovalency, covalency, and the coördinate link. In electrovalency an outer electron from one atom or group of atoms is transferred to another atom or group of atoms, the two atoms or groups being then held together by electrostatic attraction. This type of valency is often spoken of as the polar link. Thus, in forming sodium chloride, sodium gives its single outer electron, $3s^1$, to chlorine, and by this exchange the sodium ion acquires the electronic configuration of neon, $1s^2 2s^2 2p^6$, while the chloride ion completes the filling of the $3p$ orbit, $1s^2 2s^2 2p^6 3s^2 3p^6$, and then resembles argon.

In covalency, the non-polar link, the two combining atoms share electrons as in methane, which contains four covalent links. Each of these four links includes two electrons, one contributed by carbon and one by hydrogen, so that in methane carbon has assumed the electronic structure of neon and each hydrogen atom has acquired the two electrons which are characteristic of helium.

The third type of link is the coördinate link, coördinate covalency. This is identical with the covalent link except that both electrons forming a bond come from one of the two atoms which are joined together. This type of combination is exemplified in hexammineplatinic chloride, $[Pt(NH_3)_6]Cl_4$, in which the quadrivalent platinum ion, which differs from radon by twelve electrons, completes its quota of electrons by coördinating with six molecules of ammonia. In this combination each nitrogen atom contributes two shared electrons, so that within the coördination sphere the platinum has acquired the electronic configuration of radon and each nitrogen retains that of neon.

It is to be noted that the driving force in these three types of linking is a tendency on the part of the combining atoms to assume the electronic configuration of the nearest inert gas.

4. Magnetic susceptibility as an aid in examining coördination compounds

One physical method which is used to examine coördination compounds is that which measures their behavior in a magnetic field. This type of measurement affords a means of detecting the presence of singly occupied electron orbits, and such information can be of direct utility in determining the molecular complexity of compounds. It also provides a delicate criterion for the transition from electrostatic to covalent linking in complex salts.

Without going into detail on the subject of magnetism, suffice it to say here that the property of ferromagnetism, which varies with temperature and passes over into paramagnetism at the Curie point, has its origin in the parallel orientation of molecular magnets over microscopic regions of the solid. The effect is shown by the iron group metals, by some of their compounds, and by Heusler alloys. In the case of iron the magnitude of the effect is very large.

Ionic paramagnetism, which likewise varies with the temperature, is shown by the ions of the transition and rare earth metals, Cu^{2+}, Co^{2+}, Nd^{3+}. The effect is large and has its origin in the resultant spin or orbital angular momentum of incomplete electronic shells.

Metallic paramagnetism, independent of temperature, is shown by the alkali metals, by copper and silver, and by some of the carbides and nitrides. It results from the uncompensated spin of the metallic conduction electrons.

Residual paramagnetism, likewise independent of temperature, results from the uncompensated paramagnetism of complex ions. For example, the polyatomic ions, especially oxyacid ions, of transition elements, such as MnO_4^- and MnO_4^{2-}, show residual paramagnetism.

Diamagnetism, also independent of temperature, is shown by inert gas-like ions, such as Na^+, Br^-, etc., and by complex ions of the transition metals, such as $[Co(NH_3)_6]^{3+}$. Its origin is in the interaction of the magnetic field with closed electronic shells.

The magnitude of diamagnetic effects is small. Paramagnetic substances interact much more strongly with the magnetic field since each molecule or atom behaves as an elementary magnet.

5. *Effective atomic number and stability*

A particularly interesting aspect of complex formation is the manner in which the attachment of strongly coördinating groups may lead to the stabilization of a valency state, derivatives of which are otherwise unstable. A familiar and striking example of this phenomenon is found in the cobaltammines. In the presence of ammonia, the relative stabilities of the $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}$ ions are so far reversed that oxidation to the first-named state is effected by atmospheric oxygen at room temperature. The same stabilizing effect is produced by the coördination of anions, as is shown by the strong reducing properties of potassium cobaltocyanide. Both the higher and lower valency states of copper may be stabilized by appropriate coördinating groups. The instability of cupric iodide and cupric cyanide is a familiar fact. The iodide $[Cuen_2]I_2$, with one or two molecules of water of crystallization, is stable, with no tendency to revert to the cuprous state. In the case of the corresponding cyanide, stabilization of the bivalent state is not so complete, so that a derivative of both bivalent and univalent copper, $[Cuen_2][Cu(CN)_2]_2$, is obtained, the formation of which may be attributed to the competing effect of the stabilization of the cuprous state in the complex anion. The coördination of acetonitrile, thiourea, or ethylenethiourea stabilizes the cuprous state.

Univalent silver is also stabilized by coördination with sulfur compounds, for example, $[Agetu_3]Cl$ and $[Agetu_3]Br$. The bivalent state of silver is readily stabilized by coördination, particularly with pyridine derivatives. The complex argentic cations $[\mathrm{Agphenan}_2]^{2+}$ and $[\mathrm{Agdipy}_2]^{2+}$ are very stable.

The ferrous state, which in simple salts is readily oxidized by atmospheric oxygen, is strongly stabilized by coördination with dipyridyl or *o*-phenanthroline, so that the salts $[\mathrm{Fephenan}_3]\mathrm{X}_2$ and $[\mathrm{Fedipy}_3]\mathrm{X}_2$ are much more stable than the ferric salts.

The formation of the most stable complex compounds corresponds in certain cases to the acquirement by the central atom of the same "effective atomic number" as the nearest inert gas, a condition which affords a plausible explanation of the stability and properties of such compounds. In this connection three groups are of particular interest to the platinum chemist: namely, the nitrosyl group, the carbonyl group, and the cyanide group. Neutral nitric oxide has one electron more than has carbon monoxide. The formation of a metal nitrosyl compound can be regarded as invoking first the transfer of an electron from the NO group to the metal, followed by coördination of the $(\mathrm{NO})^+$ group thereby resulting. The effective atomic number of the metal atom is thereby increased, and its electrovalency, if an ion, is decreased, each by one unit. In an exactly similar way, the coördination of a $(\mathrm{CN})^-$ group raises the electrovalency by one unit. The coördination of the carbonyl group does not change the electrovalency of the central atom.

The effective atomic number of the central atom may be arrived at in several equivalent ways. For instance, in ascertaining that of the platinum atom in $[\mathrm{Pt(NH_3)_6}]\mathrm{Cl_4}$, the cationic complex may be considered.

$[\mathrm{Pt(NH_3)_6}]^{4+}$	
Pt^{4+}	74 electrons
$6\mathrm{NH_3}$ donate	12
Total E. A. N.	86 (radon configuration)
In $[\mathrm{Pt(NH_3)_2Cl_2}]$:	
Pt^{2+}	76 electrons
$2\mathrm{NH_3}$ donate	4
$2\mathrm{Cl}^-$ donate	4
Total E. A. N.	84 (2 electrons short of radon)

In this method it is necessary to know the state of valency of the central atom, which in the first example is four and in the second, two.

It is not always easy to ascertain with certainty what the state of valency is in compounds such as $\mathrm{K_2[RuCl_5NO]}$, $\mathrm{K_2[OsCl_5NO]}$, and $\mathrm{K_2[Fe(CN)_5NO]}$. If a solution containing the chloro acid of tervalent ruthenium is treated with nitric acid, the salt which is precipitated by the addition of potassium chloride is $\mathrm{K_2[RuCl_5NO]}$. In this salt, as in $\mathrm{K_2[Fe(CN)_5NO]}$, the valency of the central atom is regarded as two.

Perhaps as simple a rule as any in arriving at the effective atomic number, and incidentally, the valency of the central atom, is as follows: Each nitric oxide molecule transfers one electron to the central atom and donates two; each carbon monoxide molecule donates two electrons; each neutral molecule, such as NH_3, donates two electrons; each CN group withdraws one electron from the central atom and donates two; each chlorine atom likewise withdraws one electron and donates two. In addition, if the central atom is in the anionic complex, electrons equal in number to the unit charges on the complex are added; if the central atom is in the cationic complex, the number is subtracted in totaling the effective atomic number. A few examples may make this clear.

$Ni(CO)_4$	$28 + 8 = 36$	(Kr)
$Fe(CO)_5$	$26 + 10 = 36$	(Kr)
$Cr(CO)_6$	$24 + 12 = 36$	(Kr)
$Mo(CO)_6$	$42 + 12 = 54$	(Xe)
$Ru(CO)_5$	$44 + 10 = 54$	(Xe)
$K_2[Fe(CN)_5NO]$	$26 - 5 + 10 + 1 + 2 + 2 = 36$	(Kr)
$K_2[Ru(CN)_5NO]$	$44 - 5 + 10 + 1 + 2 + 2 = 54$	(Xe)
$K_2[RuCl_5NO]$	$44 - 5 + 10 + 1 + 2 + 2 = 54$	(Xe)
$K_2[OsCl_5NO]$	$76 - 5 + 10 + 1 + 2 + 2 = 86$	(Rn)
$K_3[Fe(CN)_5CO]$	$26 - 5 + 10 + 2 + 3 = 36$	(Kr)
$K_3[Fe(CN)_5NH_3]$	$26 - 5 + 10 + 2 + 3 = 36$	(Kr)
$K_4[Fe(CN)_6]$	$26 - 6 + 12 + 4 = 36$	(Kr)
$K_4[Ru(CN)_6]$	$44 - 6 + 12 + 4 = 54$	(Xe)
$[Pt(NH_3)_6]Cl_4$	$78 + 12 - 4 = 86$	(Rn)
$K_2[PtCl_6]$	$78 - 6 + 12 + 2 = 86$	(Rn)

The foregoing compounds, in which the central metallic atom has assumed the configuration of an inert gas, are found to be diamagnetic. Diamagnetism, apparently, is not confined solely to the full attainment of the inert-gas structure. Compounds in which the effective atomic number of the central metallic atom is two electrons short of the inert-gas configuration are likewise diamagnetic. For example,

$[Pt(NH_3)_2Cl_2]$	$78 - 2 + 4 + 4 = 84$
$[Pd(NH_3)_2Cl_2]$	$46 - 2 + 4 + 4 = 52$
$K_2[Ni(CN)_4]$	$28 - 4 + 8 + 2 = 34$
$K[AuBr_4]$	$79 - 4 + 8 + 1 = 84$

Paramagnetism is associated with unpaired electrons, such as is the case in the following:

$K_3[Fe(CN)_6]$	$26 - 6 + 12 + 3 = 35$
$[Cu(NH_3)_4]Cl_2$	$29 + 8 - 2 = 35$

It is only natural that one interested in the chemistry of the platinum metals should examine the more frequently encountered compounds with respect to the effective atomic number and stability, thus to correlate everyday experience with theoretical guidance.

Chloro salts

$K_2[PtCl_6]$	$78 - 6 + 12 + 2 = 86$	(Rn)
$K_2[PtCl_4]$	$78 - 4 + 8 + 2 = 84$	
$K_2[IrCl_6]$	$77 - 6 + 12 + 2 = 85$	
$K_3[IrCl_6]$	$77 - 6 + 12 + 3 = 86$	(Rn)
$K_2[OsCl_6]$	$76 - 6 + 12 + 2 = 84$	
$K_3[OsCl_6]$	$76 - 6 + 12 + 3 = 85$	
$K_2[OsCl_5NO]$	$76 - 5 + 10 + 1 + 2 + 2 = 86$	(Rn)
$K_2[PdCl_6]$	$46 - 6 + 12 + 2 = 54$	(Xe)
$K_2[PdCl_4]$	$46 - 4 + 8 + 2 = 52$	
$K_2[RhCl_6]$	$45 - 6 + 12 + 2 = 53$	
$K_3[RhCl_6]$	$45 - 6 + 12 + 3 = 54$	(Xe)
$K_2[RuCl_6]$	$44 - 6 + 12 + 2 = 52$	
$K_3[RuCl_6]$	$44 - 6 + 12 + 3 = 53$	
$K_2[RuCl_5NO]$	$44 - 5 + 10 + 1 + 2 + 2 = 54$	(Xe)

In general, it may be remarked that those compounds in which the effective atomic number of the central atom is odd are unstable. The tendency of chloro salts of quadrivalent iridium is to reduce to the tervalent form when dissolved. When chloro salts of quadrivalent palladium are dissolved in water, chlorine is liberated and the palladium atom becomes bivalent. Chloro salts of quadrivalent rhodium have never been prepared, the effective atomic number of rhodium in the tervalent state reaching the inert-gas number. In the case of tervalent ruthenium and osmium, the coördination of a nitrosyl group, with its transfer of one electron, completes the inert-gas configuration. As mentioned earlier, the nitroso complex of ruthenium is extremely stable.

In the analytical procedure involving the separation of base metals from platinum, iridium, rhodium, and palladium, these four metals are first converted to complex nitrite compounds. The compounds formed are:

$Na_2[Pt(NO_2)_6]$	$78 - 6 + 12 + 2 = 86$	(Rn)
$Na_3[Ir(NO_2)_6]$	$77 - 6 + 12 + 3 = 86$	(Rn)
$Na_3[Rh(NO_2)_6]$	$45 - 6 + 12 + 3 = 54$	(Xe)
$Na_2[Pd(NO_2)_4]$	$46 - 4 + 8 + 2 = 52$	

At an alkalinity of pH 8 these compounds are stable in a boiling solution. At an alkalinity approaching pH 10 the palladium compound begins to decompose, with the precipitation of a brownish deposit, and at higher alkalinities the decomposition is undoubtedly complete. The nitrite complexes of platinum, iridium, and rhodium were observed not to decompose at alkalinities of pH 12 to 13, and they are probably stable at even higher alkalinities.

Further discussion of the electronic interpretation of coördination leads naturally to hybridized orbits and quantum mechanics, subjects which are beyond the simple scope of this presentation. It is therefore recommended that the reader consult the two papers by Pauling (806) for his discussion of the nature of the chemical bond.

IX. The Literature

For the sake of convenience, the references here given are first of all divided into two groups. Those in group A are to papers which were published in the period from 1915 to 1940, and which deal with the inorganic and analytical chemistry of the platinum metals. One exception to this is made by including Chugaev's first research on the platinum metals (reference 1), because of its special significance. Within the group, the papers are arranged by nationality of origin and, so far as possible, by assembling them according to the leading authors. Under each such author, the papers are listed in chronological order. In locating the original papers and identifying them with the references, it was found that most of them were available in the Library of the National Bureau of Standards. Each paper not contained in the Bureau's library is marked with an asterisk.

The references in group B are to other publications that were necessary in the discussion of the subject matter of the paper.

A. REFERENCES TO THE PERIOD 1915 TO 1940

Russian contributions

From 1921 to 1935 practically the entire Russian literature on the platinum metals appeared in a journal created specifically for the purpose. It is known as *Annales de l'institut de platine (Leningrad)*. Twelve numbers of this journal appeared. Beginning with 1936 a new journal, entitled *Annales du secteur du platine, Institut de chimie générale (Moscow)*, displaced the former one but began its issues with No. 13 of the series. In these journals the papers are in the Russian language. In the *Comptes rendus* and in the *Bulletin of the Academy of Sciences* many of the papers are in English, German, or French, thereby making them more accessible to the average reader. Not all of the papers contained in these two journals are listed here. Such others as may interest the reader may be readily found in them.

The transliteration of the Russian names used here is in most cases that followed by *Chemical Abstracts.*

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The Committee on Analysis of the Platinum Institute consisted of S. F. Zhemchuzhniĭ, O. E. Zvyagintzev, B. G. Karpov, V. V. Lebedinskiĭ, N. I. Podkopaev, A. T. Grigoriev, and N. S. Kurnakov. It made its first report in 1926, and a second in 1932.

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